

Supporting Information for

**Evolution of Pyrrolidine-Type Asymmetric Organocatalysts by Click  
Chemistry**

*Sanzhong Luo,<sup>\*†</sup> Hui Xu,<sup>‡</sup> Xueling Mi,<sup>‡</sup> Jiuyuan Li,<sup>‡</sup> Xiaoxi Zheng,<sup>‡</sup> and Jin-Pei Cheng<sup>\*‡</sup>*

*Beijing National Laboratory for Molecular Sciences (BNLMS), Center for Molecular Science,  
Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, China and Department of  
Chemistry, State Key Laboratory of elemento-organic Chemistry, Nankai University, Tianjin,  
300071, China.*

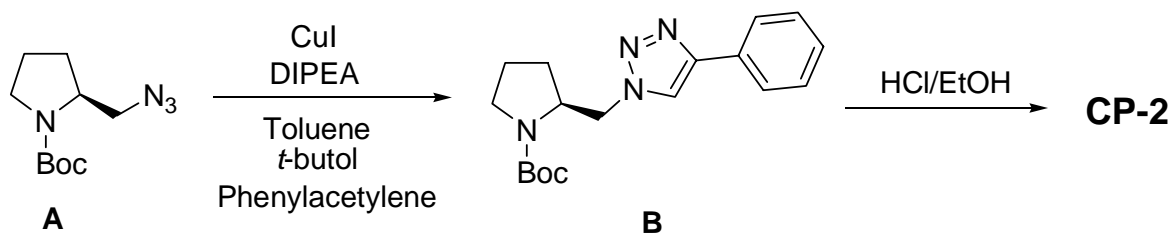
[luosz@iccas.ac.cn](mailto:luosz@iccas.ac.cn), [chengjp@mail.most.gov.cn](mailto:chengjp@mail.most.gov.cn)

General information-----	S2
Synthesis of <b>CP-1-20</b> -----	S2
General experimental procedure-----	S12
HPLC data-----	S13
NMR spectra for new compounds-----	S16
<sup>1</sup> H NMR spectra for Michael addition products-----	S36

**General Information:** Commercial reagents were used as received, unless otherwise stated. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d= doublet, t= triplet, q= quartet, h= heptet, m= multiplet, br= broad. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Mass spectra were obtained using fast-atom bombard (FAB) spectrometer or electrospray ionization (ESI) mass spectrometer. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Perkin-Elmer 341 digital polarimeter and are reported as follows:  $[\alpha]_D^{25}$  (*c* in g per 100 mL of solvent). HPLC analysis was performed using ChiralPak columns purchased.

#### Method A:

##### Synthesis of chiral catalyst CP-2:

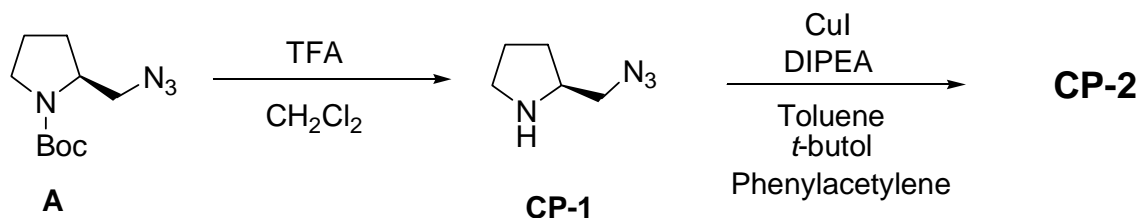


To a solution of **A** (226 mg, 1 mmol) in toluene and *t*-butanol (4mL and 1mL) was added phenylacetylene (122 mg, 1.2 mmol), CuI (10 mg, 0.05 mmol) and DIPEA (170  $\mu$ L, 2 mmol). The reaction mixture was stirred at rt overnight. After removal of the solvent under *vacuo*, the residue was purified by flash chromatograph on silica gel to afford **B** as white solid (314 mg, yield 96%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.37-1.65 (10H, m), 1.67-1.83 (1H, m), 1.89-2.07 (2H, m), 3.08-3.50 (2H, m), 4.15 (1H, s), 4.37-4.79 (2H, m), 7.29-7.38 (1H, m), 7.38-7.48 (2H, m), 7.62-7.90 (3H, m).

Chiral product **B** was deprotected in 5M HCl in ethanol to give the hydrogen chloride salts, which was subsequently dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and then treated with saturated NaHCO<sub>3</sub> solution (15 mL). This mixture was stirred for 1 hour. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL×3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in *vacuo* after filtration to give essentially pure **CP-2** as pale yellow solid (301 mg, 96%).  $[\alpha]_D^{25} = +41^\circ$  (c=1.0, CH<sub>3</sub>OH); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.35-1.52 (1H, m), 1.58-1.83 (3H, m), 1.85-1.99 (1H, m), 2.89 (2H, t, *J*= 6.6 Hz), 3.51-3.64 (1H, m), 4.11-4.21 (1H, dd, *J*= 7.9 Hz, 7.7 Hz, 13.8 Hz), 4.35-4.44 (1H, dd, *J*= 4.5 Hz, 4.3 Hz, 13.4 Hz), 7.21-7.30 (1H, t, *J*= 7.5 Hz), 7.35 (2H, t, *J*= 7.4 Hz), 7.77 (2H, t, *J*= 7.3 ), 7.86 (1H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 25.5, 29.1, 46.6, 55.5, 58.0, 120.5, 125.7, 128.0, 128.8, 130.7, 147.5; HRMS for C<sub>13</sub>H<sub>17</sub>N<sub>4</sub><sup>+</sup> (*M*+1<sup>+</sup>), calcd. 229.1448, found 229.1446.

## Method B:

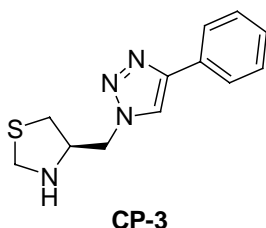
### Synthesis of chiral catalyst CP-2:



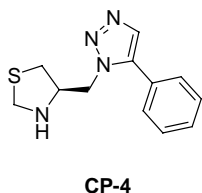
To a solution of **A** (452 mg, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added dropwise TFA (5 mL) at 0°C. The mixture was warmed to room temperature and stirred overnight. After removal of the organic solvents under *vacuo*, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and then treated with saturated NaHCO<sub>3</sub> solution (15 mL) for 1 hour at rt. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times (5 mL×3) and the combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Concentration in *vacuo* after filtration gave **CP-1** as yellow oil (438 mg, 97%).  $[\alpha]_D^{25} = -32^\circ$  (c=0.75, CHCl<sub>3</sub>) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.35-1.50 (1H, m), 1.66-2.00 (3H, m), 2.44-2.61 (1H, m), 2.86-3.04 (2H, m),

3.17-3.39 (3H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  25.5, 29.0, 46.6, 56.2, 57.7. HRMS for  $\text{C}_5\text{H}_{11}\text{N}_4^+$  ( $\text{M}+1^+$ ), calcd. 127.0984, found 127.0982.

To a solution of **CP-1** (438mg) and phenylacetylene (245 mg, 2.4 mmol) in a mixed solvent of toluene (8 mL) and *t*-butanol (2 mL) was added CuI (20 mg, 10 mmol) and DIPEA (500  $\mu\text{L}$ , 6 mmol). The reaction mixture was stirred at room temperature overnight. After removal of the solvents, the resulting residue was purified by flash chromatograph on silica gel to give **CP-2** as yellow solid (365 mg, 83%).



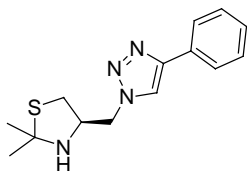
The title product was prepared according to **method A** as white solid (87% yield).  $[\alpha]_D^{25} = +10^\circ$  ( $c=0.5$ ,  $\text{CH}_3\text{OH}$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.65-2.74 (1H, dd,  $J=6.0$  Hz, 6.0 Hz, 11.4 Hz), 2.99-3.07 (1H, dd,  $J=6.4$  Hz, 6.4 Hz, 10.6 Hz), 3.82-3.94 (1H, m), 4.22 (2H, s), 4.34-4.44 (1H, dd,  $J=7.9$  Hz, 7.9 Hz, 14.1 Hz), 4.56-4.67 (1H, dd,  $J=5.0$  Hz, 5.1 Hz, 14.1 Hz), 7.29-7.37 (1H, m), 7.37-7.47 (2H, m), 7.79-7.88 (2H, m), 7.89 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  35.1, 50.4, 52.4, 63.0, 119.6, 124.7, 127.2, 127.8, 129.5, 146.8; HRMS for  $\text{C}_{12}\text{H}_{15}\text{N}_4\text{S}^+$  ( $\text{M}+1^+$ ), calcd. 247.1012, found 247.1016.



1,5-substituted triazole ring was formed following the published procedure.<sup>1</sup> To the dried flask containing a solution of EtMgBr (2 mmol) in anhydrous THF (2 mL) under a nitrogen atmosphere, phenylacetylene (204 mg, 2 mmol) was added dropwise at room temperature. After addition, the solution was heated to about 50 °C for 15 min and then cooled to room temperature. Neat (*R*)-*tert*-butyl 4-(azidomethyl)thiazolidine-3-carboxylate (244 mg, 1 mmol) was added dropwise. This reaction mixture was stirred under room temperature for 30 min, then 50 °C for 15 min. The reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  and the

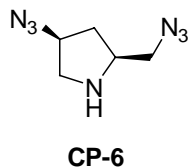
products were extracted using CH<sub>2</sub>Cl<sub>2</sub> (5 mL×3). The combined organic phase was dried over anhydrous sodium sulphate and concentrated by rotary evaporator under reduced pressure. The residue was purified by flash chromatograph on silica gel to give Boc-protected **CP-4** as pale yellow oil (310mg, 90% yield).

The Boc-protected **CP-4** was deprotected using 4M HCl dioxane solution (5 mL). Concentration in *vacuo* afforded the hydrogen chlorides salts, which was subsequently neutralized in saturated NaHCO<sub>3</sub> solution (5 mL). The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL×3). The combined extracts were dried over anhydrous sodium sulphate, and then concentrated in *vacuo* to give **CP-4** as yellow oil (90% yield).  $[\alpha]_D^{25} = -10^\circ$ , (c=0.6, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.10 (1H, s), 2.47-2.56 (1H, m), 2.79-2.88 (1H, m), 3.72-3.86 (1H, m), 3.88-3.94 (1H, dd, *J*= 2.5 Hz, 2.5 Hz, 9.6 Hz), 3.99-4.06 (1H, dd, *J*= 2.8 Hz, 2.8 Hz, 9.6 Hz), 4.35-4.53 (2H, m), 7.33-7.42 (2H, m), 7.42-7.52 (3H, m), 7.63-7.68 (1H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 36.0, 49.0, 53.3, 64.0, 126.9, 129.0, 129.1, 129.6, 133.0, 138.6; HRMS for C<sub>12</sub>H<sub>15</sub>N<sub>4</sub>S<sup>+</sup> (*M*+1<sup>+</sup>), calcd. 247.1012, found 247.1012.



**CP-5**

The title compound was prepared according to **method A** as white solid (83% yield).  $[\alpha]_D^{25} = -120.4^\circ$ , (c=0.5, CH<sub>3</sub>OH); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.54 (3H, s), 1.64 (3H, s), 1.73-2.23 (1H, br), 2.80 (1H, t, *J*= 9.8 Hz), 3.15-3.23 (1H, dd, *J*= 6.0 Hz, 5.8 Hz, 10.6 Hz), 3.80-4.02 (1H, m), 4.53-4.61 (1H, dd, *J*= 6.8 Hz, 6.6 Hz, 14.1 Hz), 4.67-4.79 (1H, dd, *J*= 4.9 Hz, 5.1 Hz, 13.9 Hz), 7.28-7.37 (1H, m), 7.37-7.49 (2H, m), 7.78-7.85 (2H, m), 7.91 (1H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 30.6, 31.6, 38.4, 51.6, 62.1, 74.2, 119.6, 124.7, 127.3, 127.9, 129.4, 146.8; HRMS for C<sub>14</sub>H<sub>19</sub>N<sub>4</sub>S<sup>+</sup> (*M*+1<sup>+</sup>), calcd. 275.1325, found 275.1329.

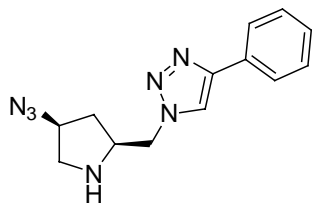


To a stirred solution of (2*S*,4*S*)-( *tert*-Butoxycarbonyl)-4-(*p*-toluenesulfonyl)-loxy)-2-[(*p*-toluenesulfonyloxy)methyl]pyrrolidine (1.44g, 1.74mmol) [*J. Org. Chem.* 1980, 45, 4728-4739] in DMF (15 mL) was added NaN<sub>3</sub> in portions at rt.

The reaction mixture was allowed to warm to 70 °C for 3 hours, and then 90 °C for 5 hours. After removal of solvent under reduced pressure, the residue was diluted in a mixture of H<sub>2</sub>O (50 mL) and ethyl acetate (15 mL). The aqueous layer was extracted by ethyl acetate (10 mL×3). The combined organic phase was dried over anhydrous sodium sulphate and concentrated by rotary evaporator. The residue was purified by flash chromatograph on silica gel to afford **Boc-protected CP-6** as colorless oil (626 mg, 86% yield).

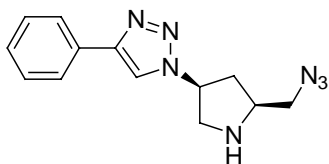
**Boc-protected CP-6** from the former step (267 mg, 1 mmol) was deprotected in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and TFA (2 mL). Concentration in *vacuo* gave the TFA salts, which was subsequently neutralized in saturated NaHCO<sub>3</sub> solution (5 mL). The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL×3). The combined organic layer was dried with anhydrous sodium sulphate and concentrated in *vacuo* to afford **CP-6** as yellow oil (166mg, 99% yield).  $[\alpha]_D^{25} = +18^\circ$ , (c=0.3, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.52-1.62 (1H, m), 1.84 (1H, s), 2.17-2.30 (1H, m), 2.27-3.11 (2H, m), 3.26-3.42 (3H, m), 3.98-4.08 (1H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 35.3, 52.6, 55.5, 57.3, 61.5; HRMS for C<sub>5</sub>H<sub>10</sub>N<sub>7</sub><sup>+</sup> (M+1<sup>+</sup>), calcd. 168.0992, found 168.0993.

The “click reaction” between **Boc-protected CP-6** with phenylacetylene afforded simultaneously three products, i.e. the Boc-protected **CP-7**, **CP-8** and **CP-9** with 19%, 14%, 40% yield, respectively. Those Boc-protected products were deprotected using the standard procedure to give the final products **CP-7**, **CP-8** and **CP-9**.



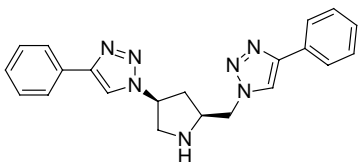
**CP-7**

Yellow solid.  $[\alpha]_D^{25} = +38.5^\circ$ , ( $c=0.36$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.58-1.68 (1H, m), 2.06 (1H, s), 2.22-2.38 (1H, m), 2.96-3.20 (2H, m), 3.64-3.78 (1H, m), 3.98-4.10 (1H, m), 4.26-4.39 (1H, m), 4.42-4.58 (1H, m), 7.27-7.37 (1H, m), 7.37-7.47 (2H, t,  $J = 7.2$  Hz), 7.78-7.87 (2H, d,  $J = 7.4$  Hz), 7.90 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  35.3, 52.2, 55.1, 57.1, 61.1, 120.7, 125.7, 128.1, 128.8, 130.6, 147.6; HRMS for  $\text{C}_{13}\text{H}_{16}\text{N}_7^+$  ( $\text{M}+1^+$ ), calcd. 270.1462, found 270.1463.



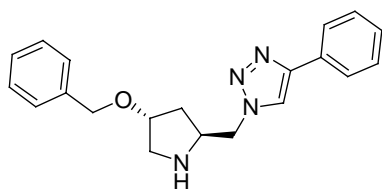
**CP-8**

Yellow solid.  $[\alpha]_D^{25} = +16.0^\circ$ , ( $c=0.5$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.90-2.09 (3H, m), 2.58-2.69 (1H, m), 3.32-3.60 (4H, m), 5.15-5.25 (1H, m), 7.29-7.37 (1H, m), 7.38-7.48 (2H, t,  $J = 7.2$  Hz), 7.84 (2H, d,  $J = 7.3$  Hz), 8.01 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  36.6, 53.6, 55.1, 57.8, 60.6, 118.1, 125.7, 128.2, 128.8, 130.6, 130.6, 148.1; HRMS for  $\text{C}_{13}\text{H}_{16}\text{N}_7^+$  ( $\text{M}+1^+$ ), calcd. 270.1462, found 270.1465.



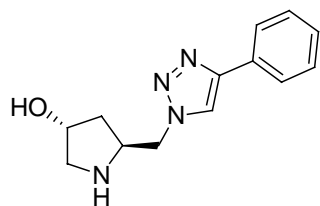
**CP-9**

White solid.  $[\alpha]_D^{25} = +16.7^\circ$ , ( $c=0.48$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.05-2.17 (2H, m), 2.65-2.78 (1H, m), 3.29-3.38 (1H, dd,  $J = 3.6$  Hz, 3.6 Hz, 11.5 Hz), 3.38-4.48 (1H, dd,  $J = 6.4$  Hz, 6.4 Hz, 11.5 Hz), 3.81-3.92 (1H, m), 4.46-4.67 (2H, m), 5.11-5.23 (1H, m), 7.29-7.46 (6H, m), 7.74-7.87 (5H, m), 7.93 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  35.2, 52.5, 53.2, 56.7, 59.3, 117.1, 119.9, 124.7, 127.1, 127.2, 127.8, 127.9, 129.4, 146.7, 147.1; HRMS for  $\text{C}_{21}\text{H}_{22}\text{N}_7^+$  ( $\text{M}+1^+$ ), calcd. 372.1931, found 372.1931.



**CP-10**

Prepared according to **method A** as colorless oil (20% yield, 79% of the starting materials were recycled).  $[\alpha]_D^{25} = +6.0^\circ$ , ( $c=0.67$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.39-1.58 (1H, m), 1.97-2.15 (2H, m), 2.75-2.85 (1H, dd,  $J=4.0$  Hz, 4.2 Hz, 12.3 Hz), 2.95-3.06 (1H, m), 3.72-3.84 (1H, m), 3.95-4.05 (1H, m), 4.10-4.20 (1H, dd,  $J=7.4$  Hz, 7.4 Hz, 14.1 Hz), 4.30-4.44 (3H, m), 7.13-7.28 (5H, m), 7.28-7.40 (3H, m), 7.72-7.78 (2H, m), 7.88 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  34.6, 51.1, 51.3, 54.1, 55.8, 69.7, 78.8, 119.6, 124.7, 126.5, 126.6, 126.7, 127.0, 127.4, 127.8, 129.7, 137.1, 146.5; HRMS for  $\text{C}_{20}\text{H}_{23}\text{N}_4\text{O}^+$  ( $M+1^+$ ), calcd. 335.1866, found 335.1867.



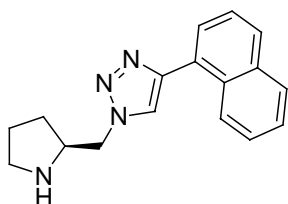
**CP-11**

(*2S,4R*)-*tert*-butyl 4-(benzyloxy)-2-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)pyrrolidine-1-carboxylate (515 mg, 1.19 mmol) was treated with Pd/C (100 mg) and methanol (15 mL) under hydrogen. The reaction mixture was stirred at 60 °C until the substrate was completely consumed by TLC. The mixture was filtered through Celite and the resulting solution was concentrated in *vacuo* to give **Boc-CP-11** as colorless oil (125 mg, 32% yield, starting materials were recycled in 65% yield).

The **Boc-CP-11** obtained from former steps was deprotected in a mixture of  $\text{CH}_2\text{Cl}_2$  (2 mL) and TFA (2 mL). After removal of solvents in *vacuo*, the resulting TFA salt was subsequently neutralized in saturated  $\text{NaHCO}_3$  solution (5 mL). The aqueous solution was extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL $\times$ 3). The combined extracts were dried over anhydrous sodium sulphate. The organic solvent was concentrated in *vacuo* to afford **CP-11** as colorless oil (82mg, 92% yield).  $[\alpha]_D^{25} = +8.0^\circ$ , ( $c=0.25$ ,

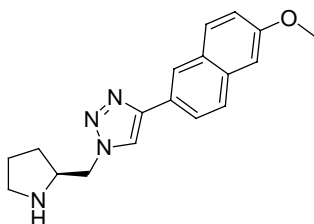


CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.57-1.72 (1H, m), 1.94-2.06 (1H, m), 2.06-2.33 (3H, m), 2.95 (1H, s), 3.89-4.02 (1H, m), 4.22-4.32 (1H, dd, *J*= 7.2 Hz, 7.5 Hz, 13.8 Hz), 4.37-4.60 (2H, m), 7.29-7.38 (1H, m), 7.38-7.49 (2H, m), 7.78-7.88 (2H, m), 7.98 (1H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 29.7, 38.8, 55.0, 56.6, 72.7, 120.7, 125.7, 128.1, 128.9, 130.7, 147.6; HRMS for C<sub>13</sub>H<sub>17</sub>N<sub>4</sub>O<sup>+</sup> (*M*+1<sup>+</sup>), calcd. 245.1397, found 245.1399.



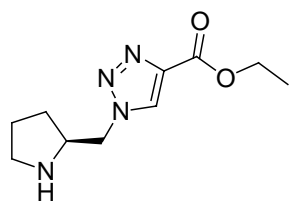
**CP-12**

The title compound was prepared according to **method A** as yellow oil (90% yield). [ $\alpha$ ]<sub>D</sub><sup>rt</sup> = +9.5°, (*c*=0.42, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.36-1.55 (1H, m), 1.55-1.82 (2H, m), 1.82-1.98 (1H, m), 2.66-2.82 (1H, m), 2.89 (2H, t, *J*= 6.2 Hz), 3.50-3.68 (1H, m), 4.18-4.31 (1H, dd, *J*= 7.9 Hz, 7.9 Hz, 13.6 Hz), 4.37-4.48 (1H, dd, *J*= 4.5 Hz, 4.5 Hz, 13.4 Hz), 7.38-7.54 (3H, m), 7.66-7.73 (1H, m), 7.95 (1H, s), 8.37-8.43 (1H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 24.9, 28.6, 46.0, 54.7, 57.4, 123.1, 124.9, 125.0, 125.5, 126.1, 126.7, 127.7, 127.9, 128.3, 130.6, 133.4, 146.0; HRMS for C<sub>17</sub>H<sub>19</sub>N<sub>4</sub><sup>+</sup> (*M*+1<sup>+</sup>), calcd. 279.1604, found 279.1606.



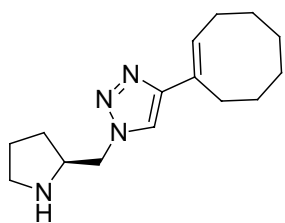
**CP-13**

The title compound was prepared according to **method A** as white solid (92% yield). [ $\alpha$ ]<sub>D</sub><sup>rt</sup> = +10.3°, (*c*=0.58, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.44-1.62 (1H, m), 1.62-1.88 (2H, m), 1.88-2.04 (1H, m), 2.92-3.02 (1H, m), 3.56-3.76 (1H, br), 3.85-3.94 (3H, m), 4.22-4.37 (1H, m), 4.39-4.51 (1H, m), 7.06-7.14 (2H, m), 7.10-7.18 (2H, m), 7.75 (2H, d, *J*= 8.5 Hz), 7.83-7.89 (1H, m), 8.00-8.06 (1H, m), 8.22 (1H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 24.4, 28.0, 45.5, 54.3, 57.2, 104.7, 118.2, 119.5, 123.1, 123.3, 126.3, 128.0, 128.7, 133.3, 146.7, 156.9; HRMS for C<sub>18</sub>H<sub>21</sub>N<sub>4</sub>O<sup>+</sup> (*M*+1<sup>+</sup>), calcd. 309.1710, found 309.1708.



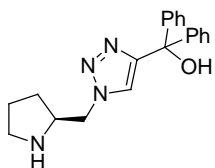
**CP-14**

The title compound was prepared according to **method A** as yellow oil (92% yield).  $[\alpha]_D^{25} = +42.9^\circ$ , ( $c=0.42$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.34 (3H, t,  $J=7.2$  Hz), 1.37-1.52 (1H, m), 1.62-1.77 (2H, m), 1.85-2.00 (1H, m), 2.80-3.00 (2H, m), 3.52-3.68 (1H, m), 4.15-4.49 (5H, m), 8.26 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  14.3, 25.5, 29.0, 46.5, 55.3, 57.7, 61.2, 128.4, 139.8, 160.8; HRMS for  $\text{C}_{10}\text{H}_{17}\text{N}_4\text{O}_2^+$  ( $\text{M}+1^+$ ), calcd. 225.1346, found 225.1346.



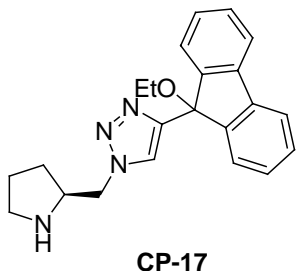
**CP-15**

The title compound was prepared according to **method A** as yellow solid (85% yield).  $[\alpha]_D^{25} = +14.5^\circ$ , ( $c=0.83$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.31-1.61 (9H, m), 1.61-1.78 (2H, m), 1.78-1.94 (1H, m), 2.11 (1H, s), 2.16-2.30 (2H, m), 2.55 (2H, t,  $J=6.3$  Hz), 2.85 (2H, t,  $J=6.6$  Hz), 3.44-3.58 (1H, m), 4.03-4.17 (1H, dd,  $J=7.9$  Hz, 7.7 Hz, 13.6 Hz), 4.24-4.35 (1H, dd,  $J=4.5$  Hz, 4.3 Hz, 13.8 Hz), 6.38 (1H, t,  $J=8.3$  Hz), 7.53 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.4, 25.0, 25.6, 25.7, 26.1, 27.8, 28.0, 29.0, 45.5, 54.3, 57.0, 118.7, 126.4, 129.4, 148.1; HRMS for  $\text{C}_{15}\text{H}_{25}\text{N}_4^+$  ( $\text{M}+1^+$ ), calcd. 261.2074, found 261.2074.

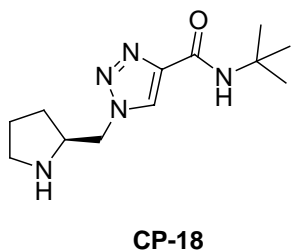


**CP-16**

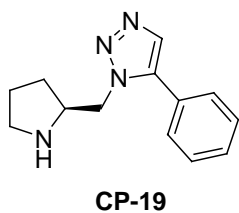
The title compound was prepared according to **method A** as yellow solid (90% yield).  $[\alpha]_D^{25} = +10.7^\circ$ , ( $c=0.75$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.23-1.39 (1H, m), 1.51-1.65 (2H, m), 1.70-1.83 (1H, m), 2.69 (2H, t,  $J=6.8$  Hz), 2.90-3.52 (3H, m), 3.96-4.08 (1H, dd,  $J=7.7\text{Hz}$ , 7.7Hz, 13.6Hz), 4.11-4.21 (1H, dd,  $J=4.9$  Hz, 4.7 Hz, 13.6 Hz), 6.85-7.45 (11H, m);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  25.2, 29.0, 46.3, 55.2, 57.7, 76.5, 123.6, 127.2, 127.3, 127.4, 127.8, 127.9, 146.1, 146.2, 153.9; HRMS for  $\text{C}_{20}\text{H}_{23}\text{N}_4\text{O}^+$  ( $\text{M}+1^+$ ), calcd. 335.1866, found 335.1866.



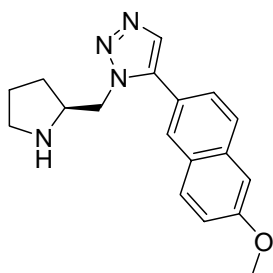
The title compound was prepared according to **method A** as yellow oil (89% yield).  $[\alpha]_D^{25} = +4.8^\circ$ , ( $c=0.83$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.00 (3H, t,  $J=7.2$  Hz), 1.24-1.39 (1H, m), 1.51-1.67 (2H, m), 1.70-1.86 (1H, m), 1.90-2.60 (1H, br), 2.69-2.85 (2H, m), 2.97 (2H, q,  $J=14.1$  Hz), 3.34-3.48 (1H, m), 3.90-4.01 (1H, m), 4.15-4.24 (1H, m), 7.14-7.35 (4H, m), 7.39 (1H, s), 7.47-7.55 (1H, m), 7.58 (3H, d,  $J=7.3$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  15.7, 25.2, 29.0, 46.4, 55.4, 57.8, 59.2, 83.8, 120.0, 122.3, 125.5, 128.0, 129.3, 140.5, 145.2, 149.7; HRMS for  $\text{C}_{22}\text{H}_{25}\text{N}_4\text{O}^+$  ( $M+1^+$ ), calcd. 361.2023, found 361.2025.



The title compound was prepared according to **method A** as white solid (95% yield).  $[\alpha]_D^{25} = +10.9^\circ$ , ( $c=0.92$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.32-1.48 (10H, m), 1.60-1.79 (2H, m), 1.83-1.97 (1H, m), 2.00-2.40 (1H, br), 2.85-2.95 (2H, m), 3.47-3.62 (1H, m), 4.15-4.25 (1H, dd,  $J=7.7$  Hz, 7.5 Hz, 13.6 Hz), 4.34-4.43 (1H, dd,  $J=4.7$  Hz, 4.7 Hz, 13.6 Hz), 6.99 (1H, s), 8.15 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.5, 27.9, 28.0, 45.5, 50.4, 54.6, 56.7, 124.8, 143.1, 158.5; HRMS for  $\text{C}_{12}\text{H}_{22}\text{N}_5\text{O}^+$  ( $M+1^+$ ), calcd. 252.1819, found 252.1820.



**CP-19** was prepared following the similar procedure with that of **CP-4** to give a yellow oil (84% yield).  $[\alpha]_D^{25} = +3.4^\circ$ , ( $c=0.58$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.28-1.43 (1H, m), 1.61-1.76 (2H, m), 1.76-1.89 (1H, m), 1.96-2.33 (1H, br), 2.88 (2H, t,  $J=6.6$  Hz), 3.54-3.78 (1H, m), 4.14-4.35 (1H, m), 7.38-7.54 (5H, m), 7.67 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.1, 28.1, 45.2, 51.9, 56.8, 126.2, 128.0, 128.1, 128.4, 131.9, 137.3; HRMS for  $\text{C}_{13}\text{H}_{17}\text{N}_4^+$  ( $M+1^+$ ), calcd. 229.1448, found 229.1447.

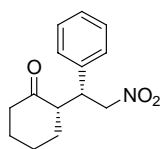


**CP-20**

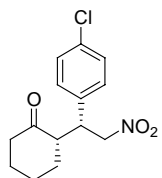
CP-20 was prepared following the similar procedure with that of **CP-4** to give a yellow oil (63% yield).  $[\alpha]_D^{25} = -3.0^\circ$ , ( $c=0.67$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.31-1.45 (1H, m), 1.61-1.77 (2H, m), 1.77-1.90 (1H, m), 1.94-2.37 (1H, br), 2.91 (2H, t,  $J=6.8$  Hz), 3.61-3.78 (1H, m), 3.95 (3H, s), 4.20-4.40 (2H, m), 7.11-7.25 (2H, m), 7.48 (1H, d,  $J=8.1$  Hz), 7.70-7.86 (3H, m), 7.90 (1H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  24.1, 28.1, 45.3, 52.0, 54.4, 56.8, 104.6, 118.9, 121.0, 125.6, 126.6, 127.5, 128.7, 132.0, 133.6, 137.5, 157.6; HRMS for  $\text{C}_{18}\text{H}_{21}\text{N}_4\text{O}^+$  ( $M+1^+$ ), calcd. 309.1710, found 309.1710.

**Procedure for the Michael reaction:** Nitrostyrene (37 mg, 0.25 mmol) and **CP-2** (12 mg, 10 mol%) were mixed with cyclohexanone (0.5 mL, 5 mmol) in the presence of TFA (0.00625 mmol, 0.2  $\mu\text{L}$ ) at room temperature (Bulk solution of TFA in cyclohexanone was freshly prepared and employed in the reaction, 20  $\mu\text{L}$  TFA in 50 mL of cyclohexanone). The homogeneous reaction mixture was stirred at room temperature for 18 h. The reaction mixture was directly loaded onto silica gel column to afford the Michael adduct **1** (61 mg, 99%) as white solid:  $[\alpha]_D^{25} = -15.2^\circ$  ( $c=0.5$ ,  $\text{CH}_3\text{OH}$ ), *syn/anti*=49:1 (by  $^1\text{H}$  NMR), 92% *ee* (by HPLC on a chiral phase chiralpak AD-H column,  $\lambda=254$  nm, *i*PrOH/hexane 10:90, 20  $^\circ\text{C}$ , 0.5 mL  $\text{min}^{-1}$ ;  $t_R=22.7$  min (minor), 29.4 min (major)). All the Michael addition products are known compounds.<sup>2-5</sup>

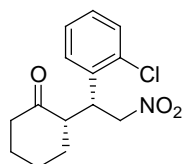
**HPLC conditions:**



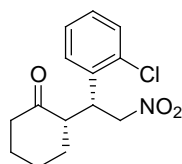
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=10:90), 25 °C, 0.5 mL/min;  $t_R$ = 22.7 min (minor), 29.4 min (major).



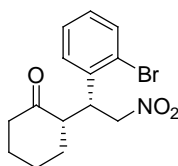
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=10:90), 20 °C, 0.5 mL/min;  $t_R$ = 27.4 min (minor), 41.6 min (major).



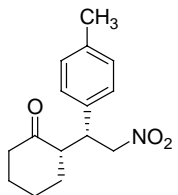
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=10:90), 20 °C, 0.5 mL/min;  $t_R$ = 27.4 min (minor), 41.6 min (major).



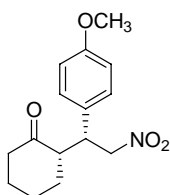
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=10:90), 20 °C, 0.5 mL/min;  $t_R$ = 27.4 min (minor), 41.6 min (major).



The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=10:90), 20 °C, 0.5 mL/min;  $t_R$ = 21.9 min (minor), 38.3 min (major).

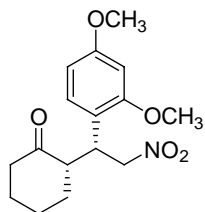


The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=10:90), 20 °C, 0.5 mL/min;  $t_R$ = 18.0 min (minor), 23.5 min (major).

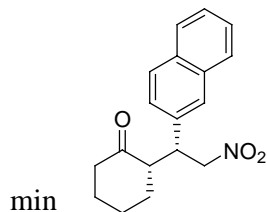


The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=20:80), 20 °C, 0.5 mL/min;  $t_R$ = 19.1 min (minor), 23.9 min (major).

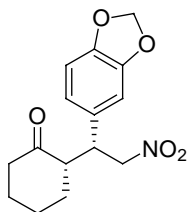
min (major).



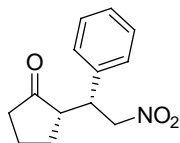
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=20:80), 20 °C, 0.5 mL/min;  $t_R$ = 17.4 min (minor), 18.9 min (major).



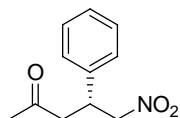
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=20:80), 20 °C, 0.5 mL/min;  $t_R$ = 20.5 min (minor), 23.9 min (major).



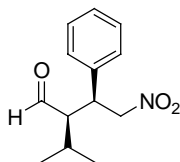
The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=20:80), 20 °C, 0.5 mL/min;  $t_R$ = 23.2 min (minor), 24.7 min (major).



The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=20:80), 20 °C, 0.5 mL/min;  $t_R$ = 13.7 min (*anti*, major), 15.1 min (*anti*, minor), 16.2 min (*syn*, minor), 20.5 min (*syn*, major).



The enantiomeric excess was determined by HPLC with an AD-H column at 254 nm (2-propanol: hexane=20:80), 20 °C, 0.5 mL/min;  $t_R$ = 14.5 min (minor), 15.4 min (major)



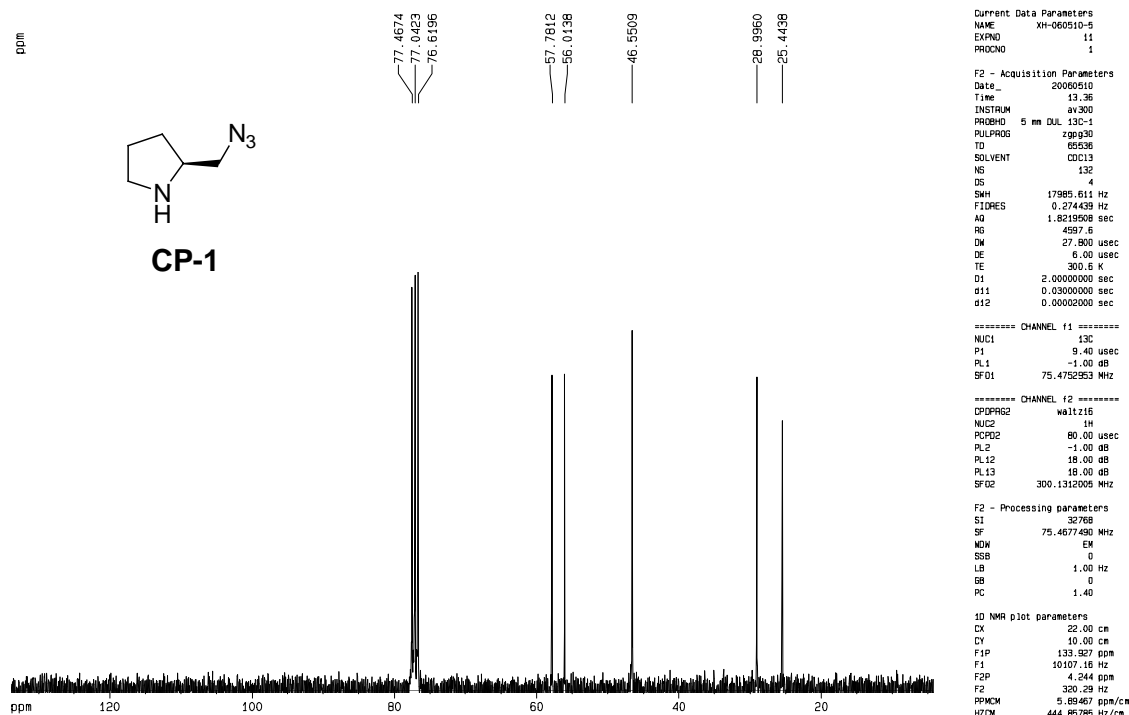
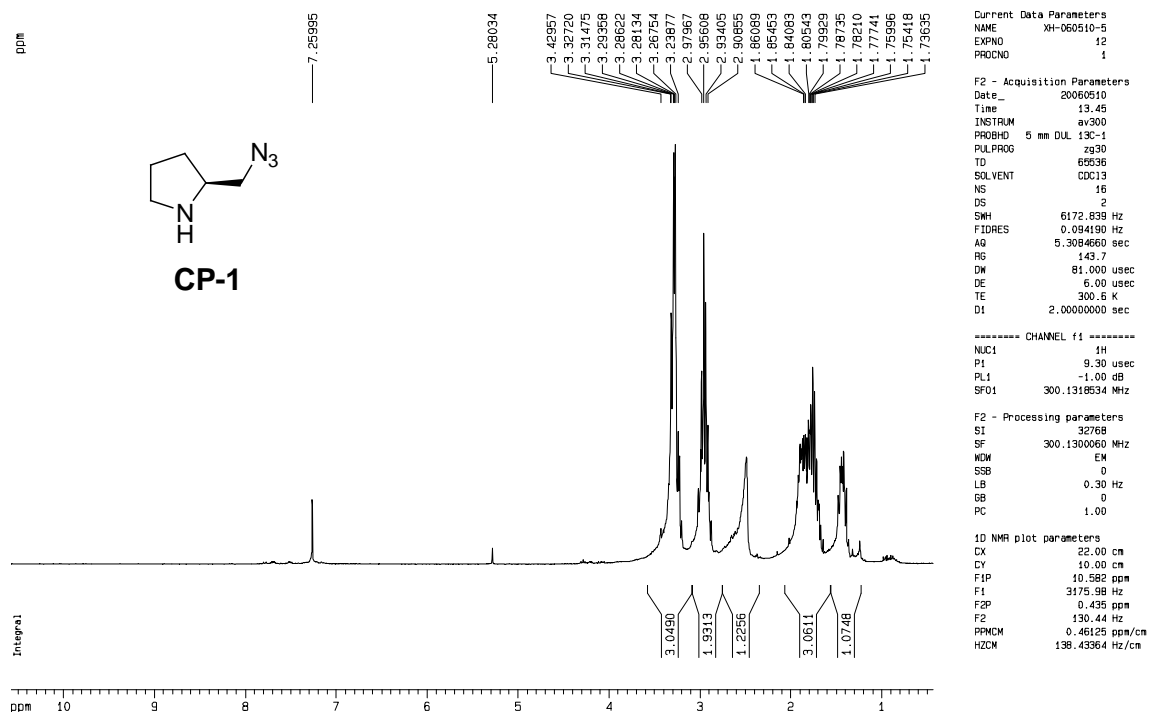
The enantiomeric excess was determined by HPLC with an AD-H column at 281 nm (2-propanol: hexane=3:97), 20 °C, 0.5 mL/min;  $t_R$ = 17.9 min (major), 21.0 min (minor)

## Reference:

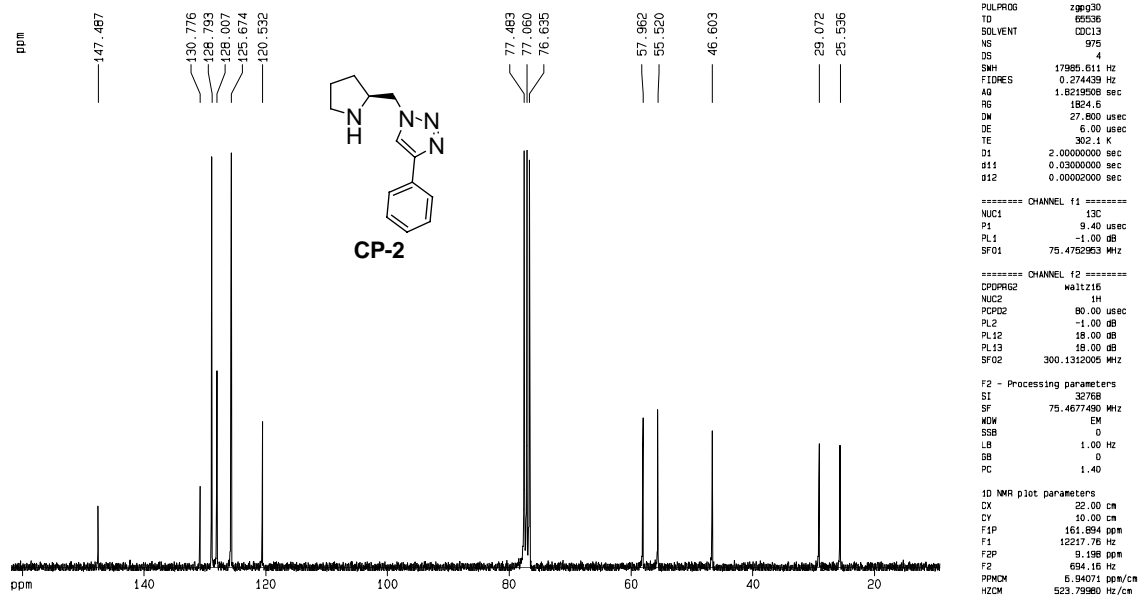
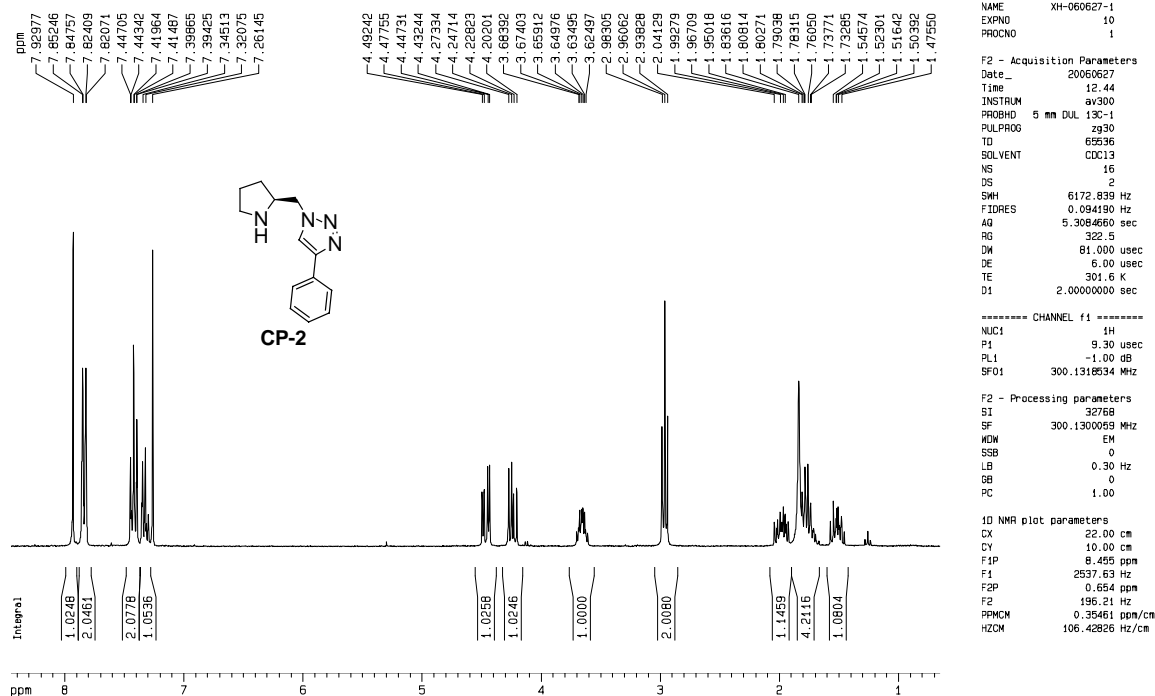
[1] Krasinski, A.; Fokin V. V.; Sharpless, K. B. *Org. Lett.* **2004**, 6, 1237.

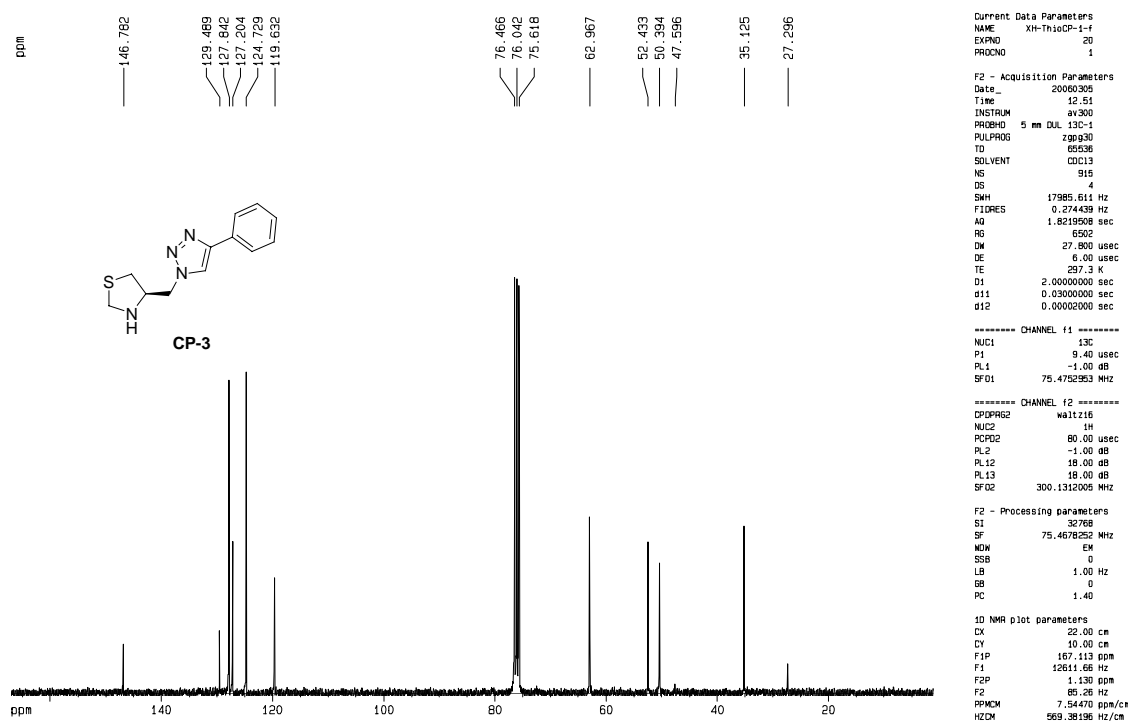
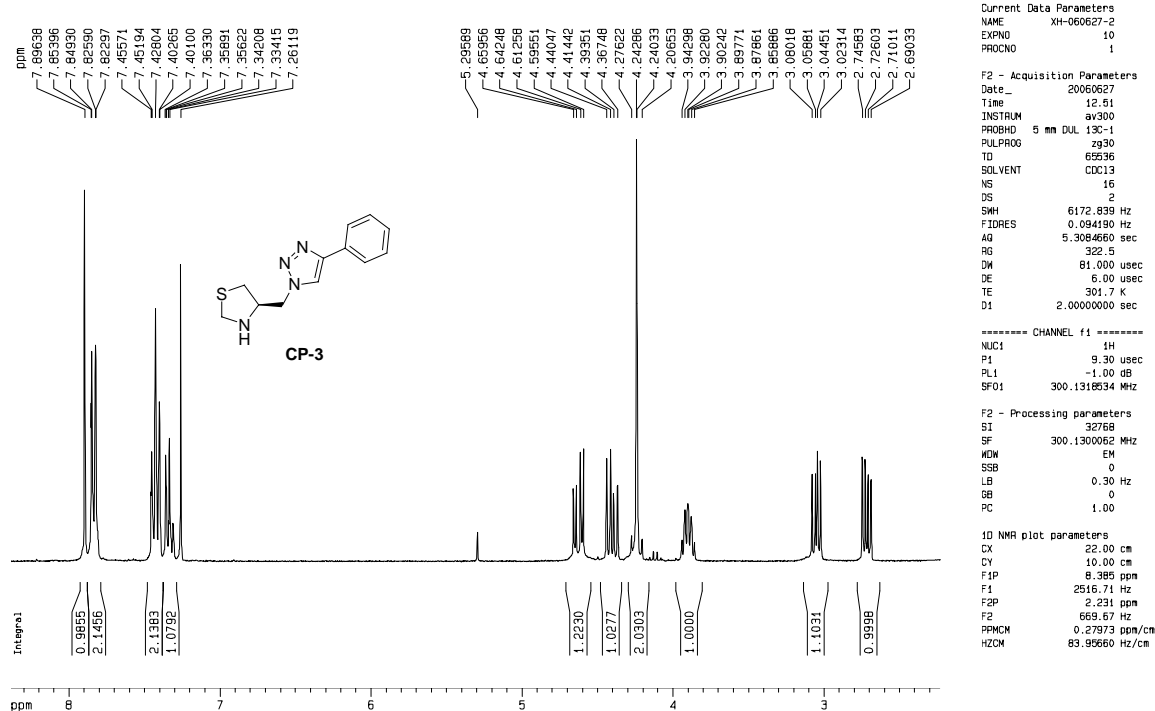
- [2] Luo, S.; Mi, X.; Zhang, L.; Liu, S.; Xu, H.; Cheng, J.-P. *Angew. Chem. Int. Ed.* **2006**, *45*, 3093 □
- [3] (a) Ishii, T.; Fujioka, S.; Sekiguchi, Y.; Kotsuki, H. *J. Am. Chem. Soc.* **2004**, *126*, 9558-9559; (b) Betancort, J. M.; Sakthivel, K.; Thayumanavan, R.; Tanaka, F.; Barbas, C. F. III, *Synthesis* **2004**, 1509-1521. (c) List, B.; Pojarliev, P.; J. Martin, H. *Org. Lett.* **2001**, *3*, 2423-2425.
- [4] (a) Cobb, A. J. A.; Longbottom, D. A.; Shaw, D. M.; Ley, S. V. *Chem. Commun.* **2004**, 1808-1809; (b) Cobb, A. J. A.; Shaw, D. M.; Longbottom, D. A.; Gold, J. B.; Ley, S. V. *Org. Biomol. Chem.* **2005**, *3*, 84-96;
- [5] (a) Wang, W.; Wang, J.; Li, H. *Angew. Chem. Int. Ed.* **2005**, *44*, 1369; (b) Hayashi, Y.; Gotoh, H.; Hayashi, T.; Shoji, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 4212-4215.

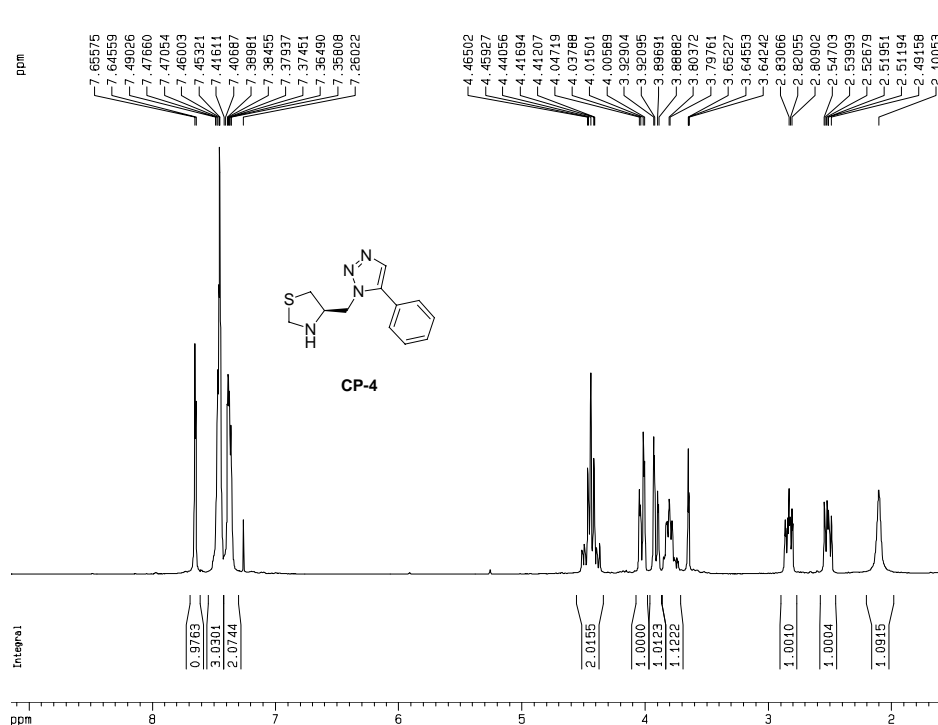
# NMR spectra for the clicked catalysts











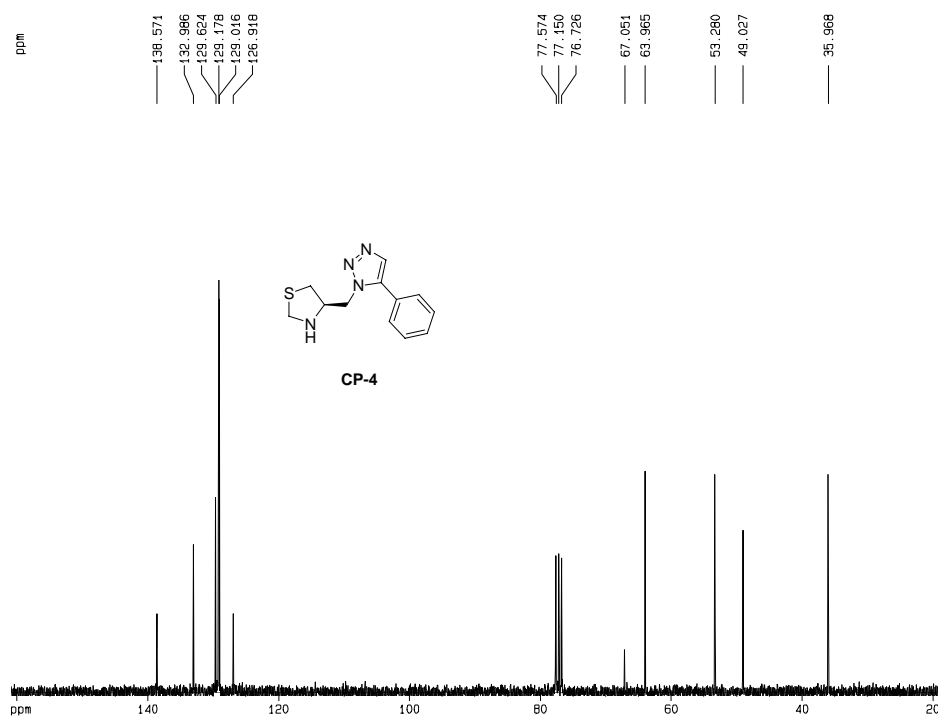
Current Data Parameters  
NAME XH-060316-2  
EXPNO 10  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20060316  
Time 13.39  
INSTRUM av300  
PROBHD 5 mm DUL 13C-1  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 6172.839 Hz  
FIDRES 0.094190 Hz  
AQ 5.3084660 sec  
RG 101.6  
DM 81.000 usec  
DE 6.00 usec  
TE 299.5 K  
D1 2.00000000 sec

----- CHANNEL f1 -----  
NUC1 1H  
P1 9.30 usec  
PL1 -1.00 dB  
SFO1 300.1318534 MHz

F2 - Processing parameters  
SI 32768  
SF 300.1300062 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

1D NMR plot parameters  
CX 22.00 cm  
CY 10.00 cm  
F1P 9.151 ppm  
F1 2746.56 Hz  
F2P 1.524 ppm  
F2 457.30 Hz  
P1MCH 0.34671 ppm/cm  
HZCM 104.05750 Hz/cm



Current Data Parameters  
NAME XH-060316-2  
EXPNO 11  
PROCNO 1

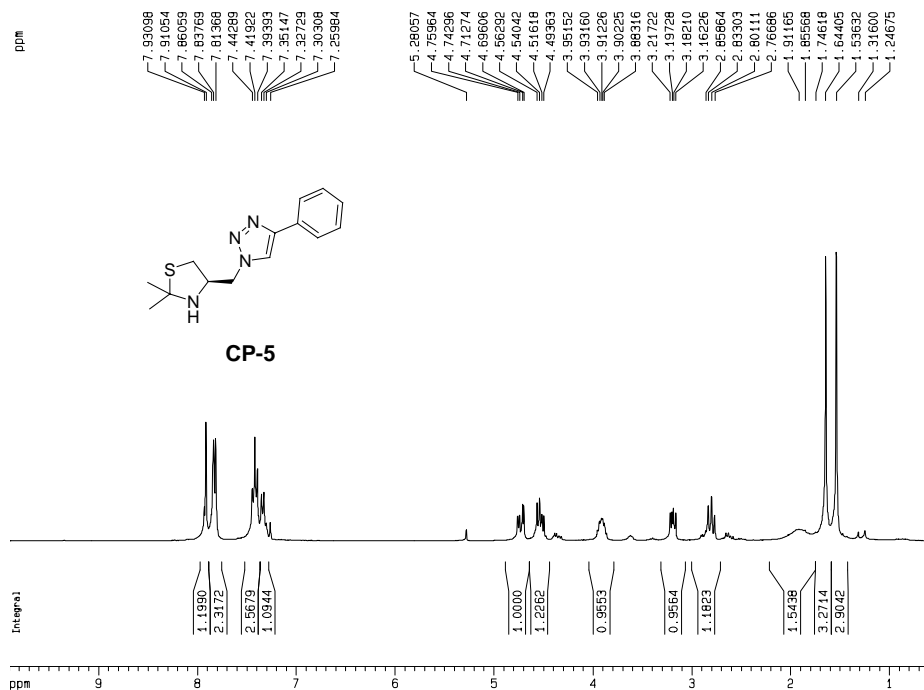
F2 - Acquisition Parameters  
Date\_ 20060316  
Time 13.41  
INSTRUM av300  
PROBHD 5 mm DUL 13C-1  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 41  
DS 4  
SWH 17989.611 Hz  
FIDRES 0.274438 Hz  
AQ 1.8219508 sec  
RG 3649.1  
DM 27.800 usec  
DE 6.00 usec  
TE 299.7 K  
D1 2.00000000 sec  
d11 0.03000000 sec  
d12 0.00000000 sec

----- CHANNEL f1 -----  
NUC1 13C  
P1 9.40 usec  
PL1 -1.00 dB  
SFO1 75.4752953 MHz

----- CHANNEL f2 -----  
CPDPRG2 Waltz16  
NUC2 1H  
PCPD2 80.00 usec  
PL2 -1.00 dB  
PL12 18.00 dB  
PL13 18.00 dB  
SFO2 300.1312005 MHz

F2 - Processing parameters  
SI 32768  
SF 75.4677490 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

1D NMR plot parameters  
CX 24.00 cm  
CY 10.00 cm  
F1P 160.365 ppm  
F1 12147.66 Hz  
F2P 7.129 ppm  
F2 538.00 Hz  
P1MCH 61.40584 ppm/cm  
HZCM 483.73657 Hz/cm



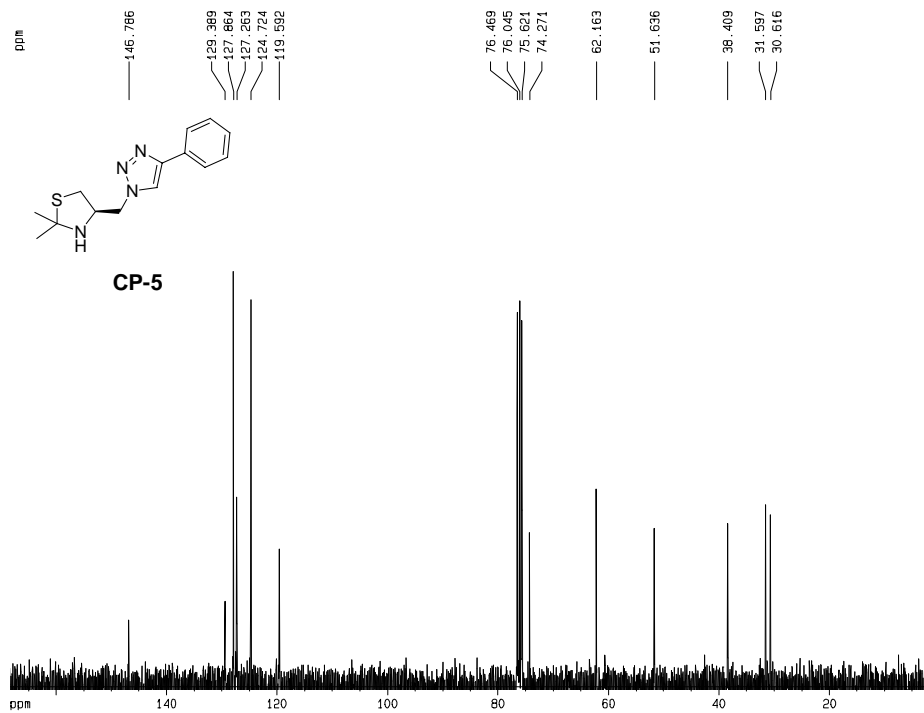
Current Data Parameters  
NAME XH-060406-1  
EXPNO 10  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20060405  
Time 21.00  
INSTRUM av300  
PROBHD 5 mm DUL 13C-1  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 6172.839 Hz  
FIDRES 0.094190 Hz  
AQ 5.3084660 sec  
RG 143.7  
DM 81.000 usec  
DE 6.00 usec  
TE 298.2 K  
D1 2.00000000 sec

===== CHANNEL f1 =====  
NUC1 1H  
P1 9.30 usec  
PL1 -1.00 dB  
SF01 300.1318534 MHz

F2 - Processing parameters  
SI 32768  
SF 300.1300062 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

1D NMR plot parameters  
CX 22.00 cm  
CY 10.00 cm  
F1 9.900 ppm  
F1 2971.40 Hz  
F2 0.570 ppm  
F2 171.14 Hz  
PMCM 0.42410 ppm/cm  
HZCM 127.28462 Hz/cm



Current Data Parameters  
NAME XH-060406-1  
EXPNO 11  
PROCNO 1

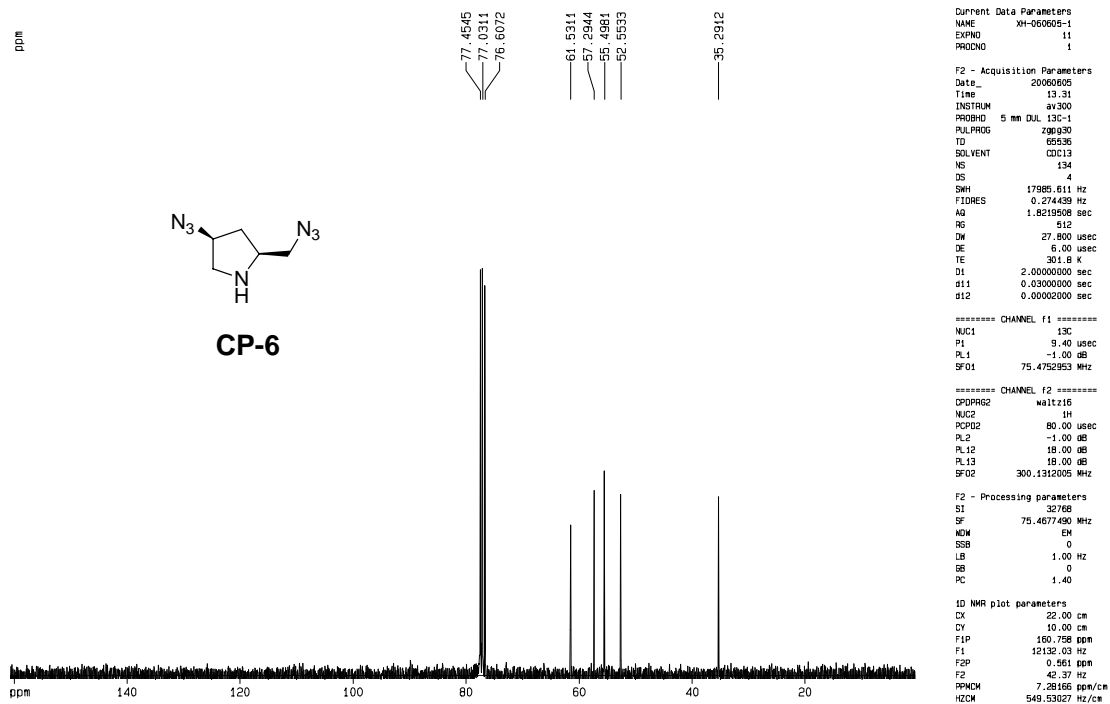
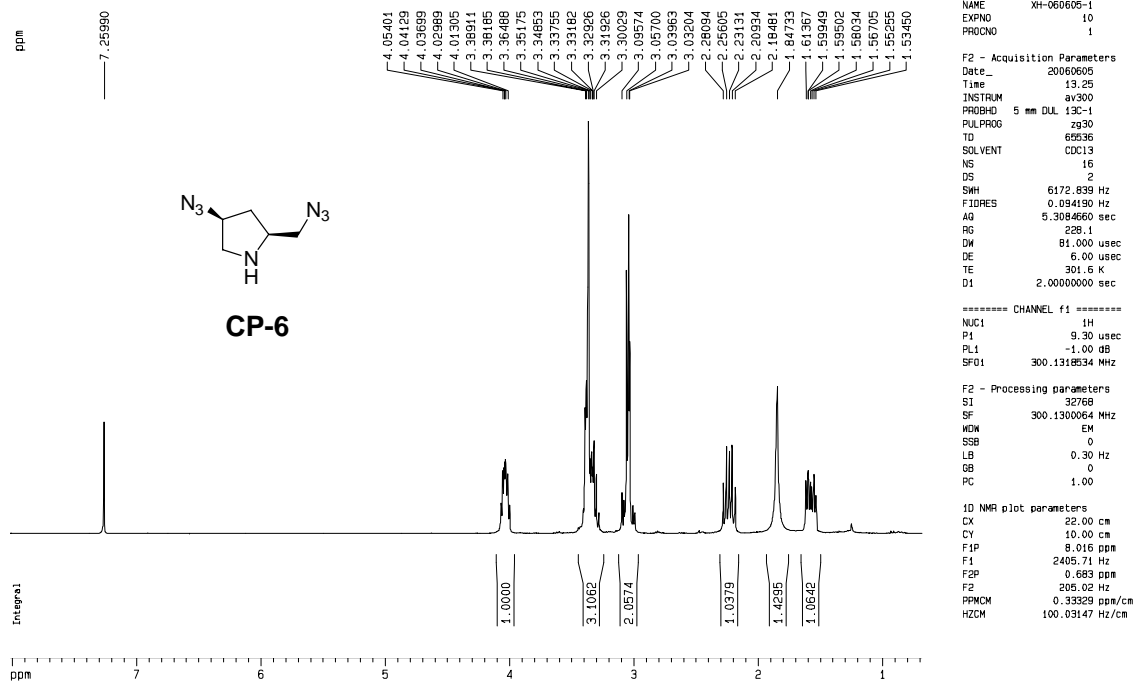
F2 - Acquisition Parameters  
Date\_ 20060405  
Time 21.02  
INSTRUM av300  
PROBHD 5 mm DUL 13C-1  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 49  
DS 4  
SWH 17985.611 Hz  
FIDRES 0.274439 Hz  
AQ 1.8219508 sec  
RG 3649.1  
DM 27.800 usec  
DE 6.00 usec  
TE 298.3 K  
D1 2.00000000 sec  
d11 0.03000000 sec  
d12 0.00020000 sec

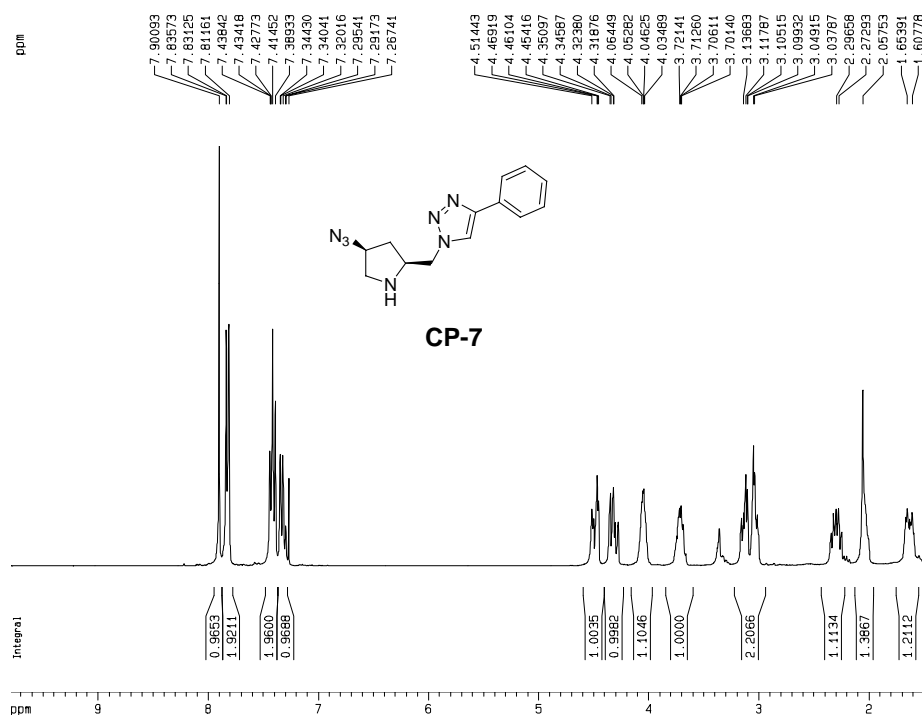
===== CHANNEL f1 =====  
NUC1 13C  
P1 9.40 usec  
PL1 -1.00 dB  
SF01 75.4752953 MHz

===== CHANNEL f2 =====  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 80.00 usec  
PL2 -1.00 dB  
PL12 18.00 dB  
PL13 18.00 dB  
SF02 300.1312005 MHz

F2 - Processing parameters  
SI 32768  
SF 75.4678262 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

1D NMR plot parameters  
CX 22.00 cm  
CY 10.00 cm  
F1 168.415 ppm  
F1 12709.32 Hz  
F2 1.379 ppm  
F2 104.11 Hz  
PMCM 7.55252 ppm/cm  
HZCM 572.99133 Hz/cm



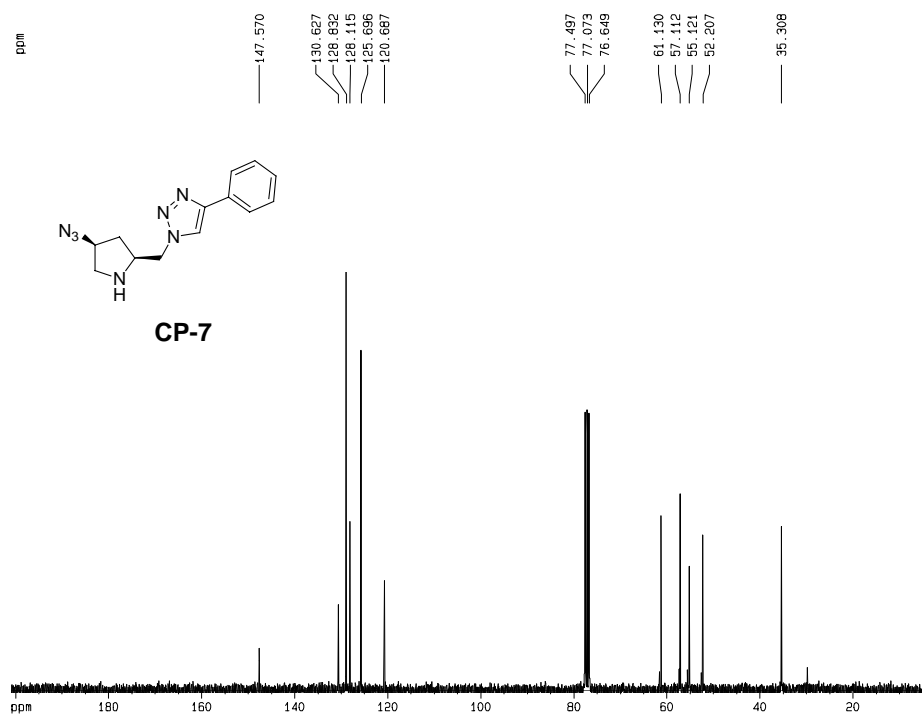


Current Data Parameters  
 NAME XH-050621-2  
 EXPNO 10  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20060622  
 Time 13.09  
 INSTRUM av300  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 6172.839 Hz  
 FIDRES 0.094190 Hz  
 AQ 5.3084660 sec  
 RG 143.7  
 DM 81.000 usec  
 DE 6.00 usec  
 TE 300.9 K  
 D1 2.00000000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 9.30 usec  
 PL1 -1.00 dB  
 SFO1 300.1318534 MHz

F2 - Processing parameters  
 SI 32768  
 SF 300.1300041 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 10.00 cm  
 F1P 9.794 ppm  
 F1 2939.46 Hz  
 F2P 1.417 ppm  
 F2 425.36 Hz  
 PPMCM 0.38076 ppm/cm  
 HZCM 114.27744 Hz/cm



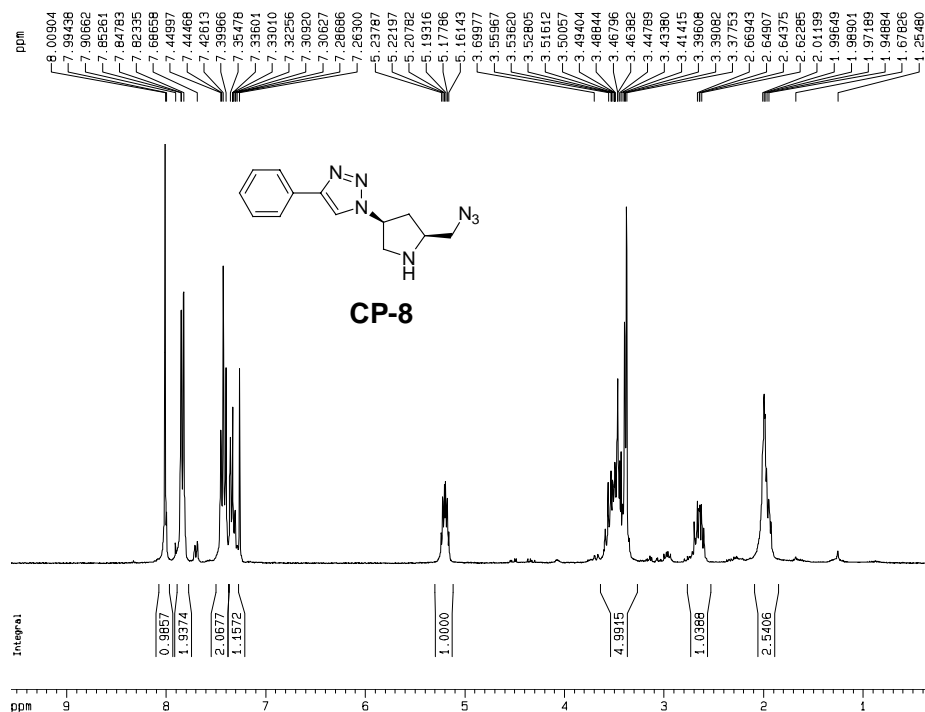
Current Data Parameters  
 NAME XH-050621-2  
 EXPNO 11  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20060622  
 Time 13.11  
 INSTRUM av300  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 239  
 DS 4  
 SWH 17985.611 Hz  
 FIDRES 0.274439 Hz  
 AQ 1.8219508 sec  
 RG 5160.6  
 DM 27.800 usec  
 DE 6.00 usec  
 TE 301.0 K  
 D1 2.00000000 sec  
 d11 0.03000000 sec  
 d12 0.00020000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 9.40 usec  
 PL1 -1.00 dB  
 SFO1 75.4752953 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 DDPGPG2 waltz16  
 NUC2 1H  
 P2P2 80.00 usec  
 PL2 -1.00 dB  
 PL12 18.00 dB  
 PL13 18.00 dB  
 SFO2 300.1312005 MHz

F2 - Processing parameters  
 SI 32768  
 SF 75.4677490 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

1D NMR plot parameters  
 CX 22.00 cm  
 CY 10.00 cm  
 F1P 201.004 ppm  
 F1 15169.34 Hz  
 F2P 2.666 ppm  
 F2 201.18 Hz  
 PPMCM 9.01539 ppm/cm  
 HZCM 680.37091 Hz/cm



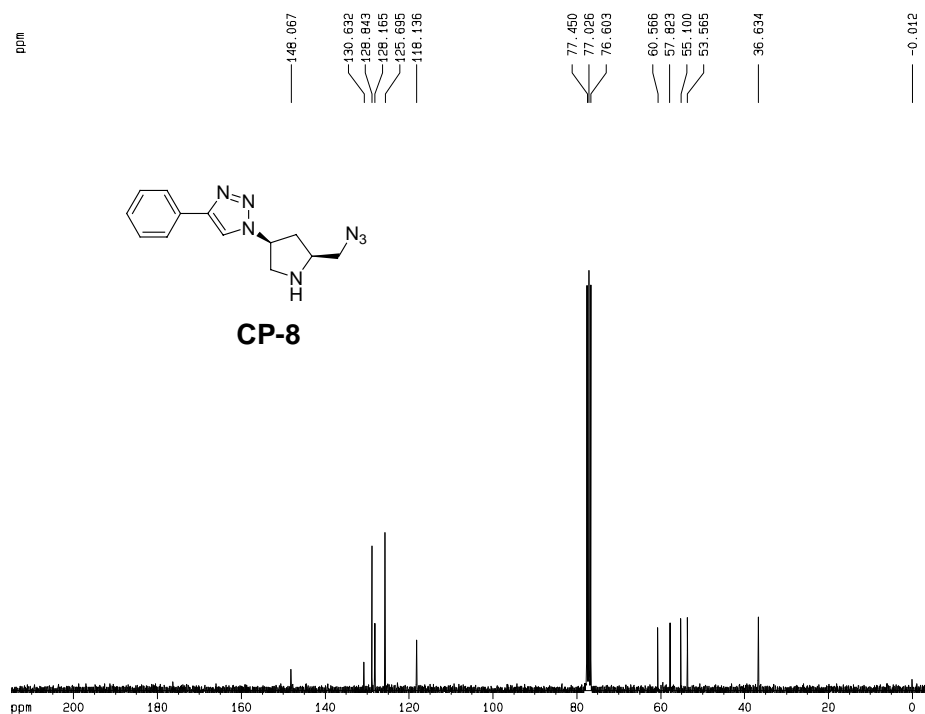
Current Data Parameters  
 NAME XH-050621-1  
 EXPNO 12  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20060522  
 Time 12.30  
 INSTRUM av300  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 6172.839 Hz  
 FIDRES 0.054190 Hz  
 AQ 5.3084660 sec  
 RG 228.1  
 DW 81.000 usec  
 DE 6.00 usec  
 TE 300.4 K  
 D1 2.00000000 sec

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 9.30 usec  
 PL1 -1.00 dB  
 SFO1 300.1318534 MHz

F2 - Processing parameters  
 SI 32768  
 SF 300.1300056 MHz  
 WDM EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 10.00 cm  
 F1P 9.562 ppm  
 F1 2869.79 Hz  
 F2P 0.300 ppm  
 F2 89.97 Hz  
 PPMCM 0.42100 ppm/cm  
 HZCM 126.35954 Hz/cm



Current Data Parameters  
 NAME XH-050621-1  
 EXPNO 13  
 PROCNO 1

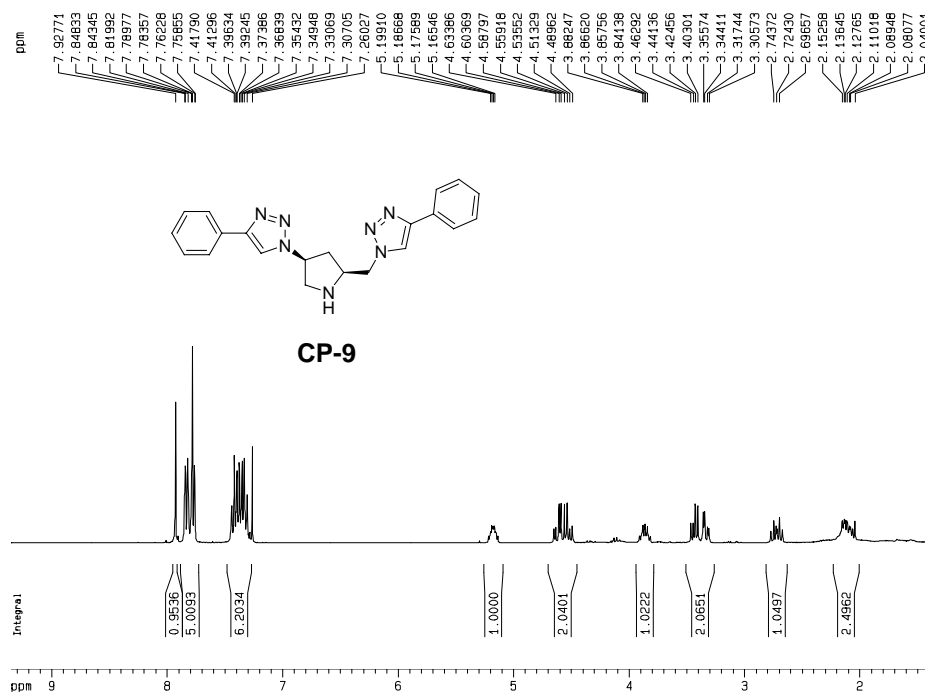
F2 - Acquisition Parameters  
 Date\_ 20060522  
 Time 12.35  
 INSTRUM av300  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 482  
 DS 4  
 SWH 17985.611 Hz  
 FIDRES 0.274439 Hz  
 AQ 1.8219508 sec  
 RG 7298.2  
 DW 27.800 usec  
 DE 6.00 usec  
 TE 300.8 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 D12 0.00002000 sec

===== CHANNEL f1 =====  
 NUC1 13C  
 P1 9.40 usec  
 PL1 -1.00 dB  
 SFO1 75.4752953 MHz

===== CHANNEL f2 =====  
 DPDPFG2 waltz16  
 NUC2 1H  
 P2P2 80.00 usec  
 PL2 -1.00 dB  
 PL12 18.00 dB  
 PL13 18.00 dB  
 SFO2 300.1312005 MHz

F2 - Processing parameters  
 SI 32768  
 SF 75.4677495 MHz  
 WDM EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

1D NMR plot parameters  
 CX 22.00 cm  
 CY 10.00 cm  
 F1P 215.000 ppm  
 F1 16225.57 Hz  
 F2P -5.000 ppm  
 F2 -377.34 Hz  
 PPMCM 10.00000 ppm/cm  
 HZCM 754.67749 Hz/cm



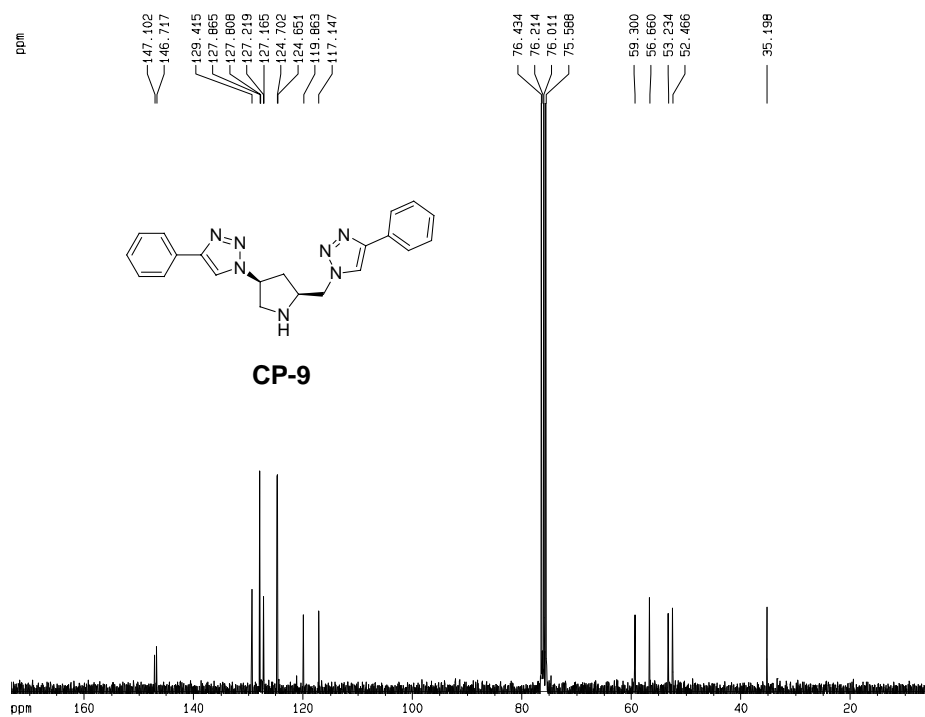
Current Data Parameters  
NAME XH-060413-1  
EXPNO 10  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20060414  
Time 12.15  
INSTRUM av300  
PROBHD 5 mm DUL 13C-1  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 6172.839 Hz  
FIDRES 0.094190 Hz  
AQ 5.3084660 sec  
RG 228.1  
DM 81.000 usec  
DE 6.00 usec  
TE 298.6 K  
D1 2.00000000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
NUC1 1H  
P1 9.30 usec  
PL1 -1.00 dB  
SF01 300.1318534 MHz

F2 - Processing parameters  
SI 32768  
SF 300.1300062 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

1D NMR plot parameters  
CX 22.00 cm  
CY 50.00 cm  
F1P 9.356 ppm  
F1 2807.88 Hz  
F2P 1.356 ppm  
F2 409.60 Hz  
PMCM 0.36322 ppm/cm  
HZCM 109.01263 Hz/cm



Current Data Parameters  
NAME XH-060413-1  
EXPNO 11  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20060414  
Time 12.19  
INSTRUM av300  
PROBHD 5 mm DUL 13C-1  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 484  
DS 4  
SWH 17985.511 Hz  
FIDRES 0.274439 Hz  
AQ 1.8219508 sec  
RG 143.7  
DM 27.800 usec  
DE 6.00 usec  
TE 298.6 K  
D1 2.00000000 sec  
d11 0.03000000 sec  
d12 0.00002000 sec

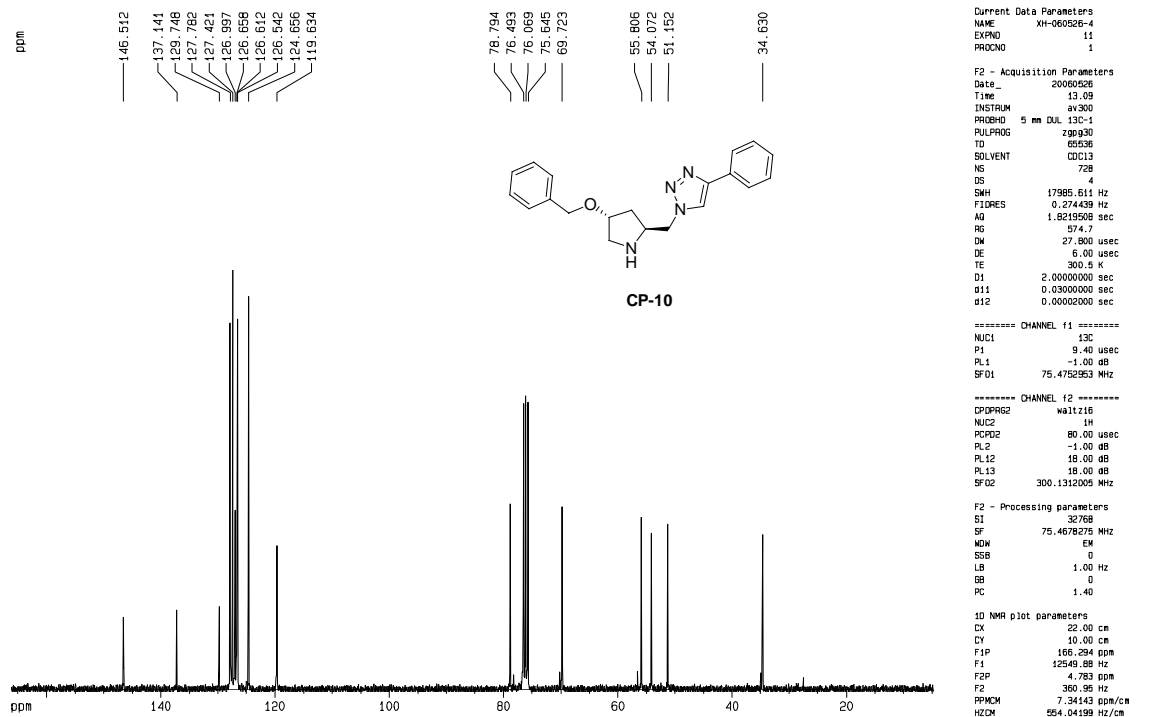
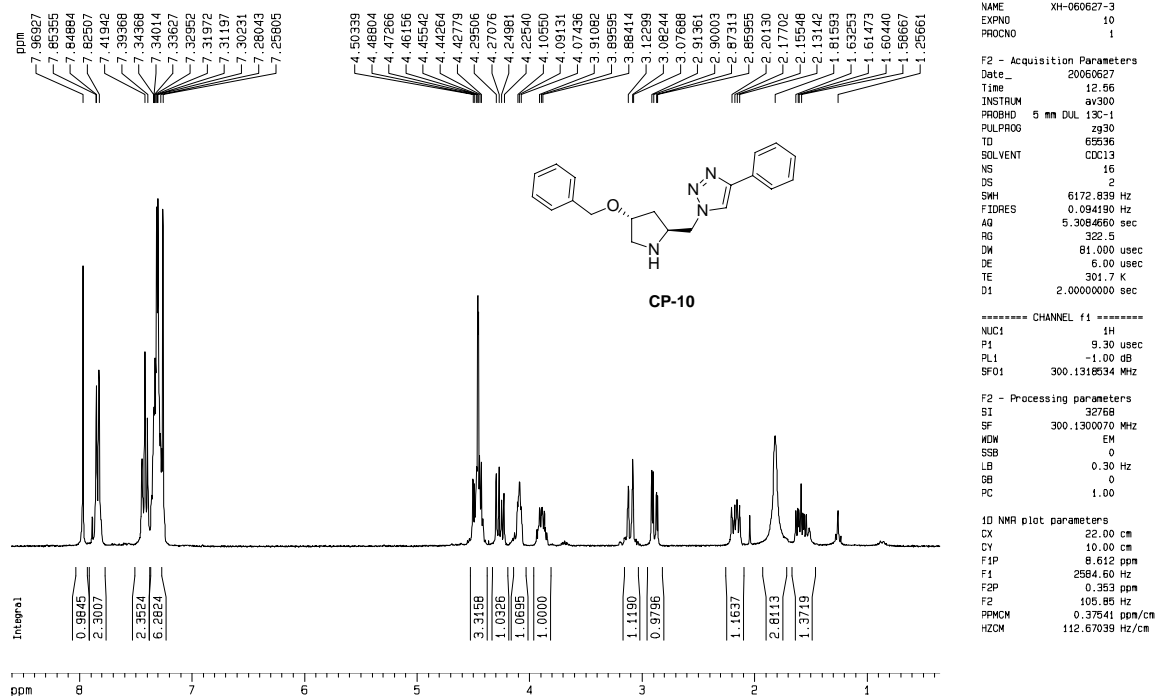
\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
NUC1 13C  
P1 9.40 usec  
PL1 -1.00 dB  
SF01 75.4752953 MHz

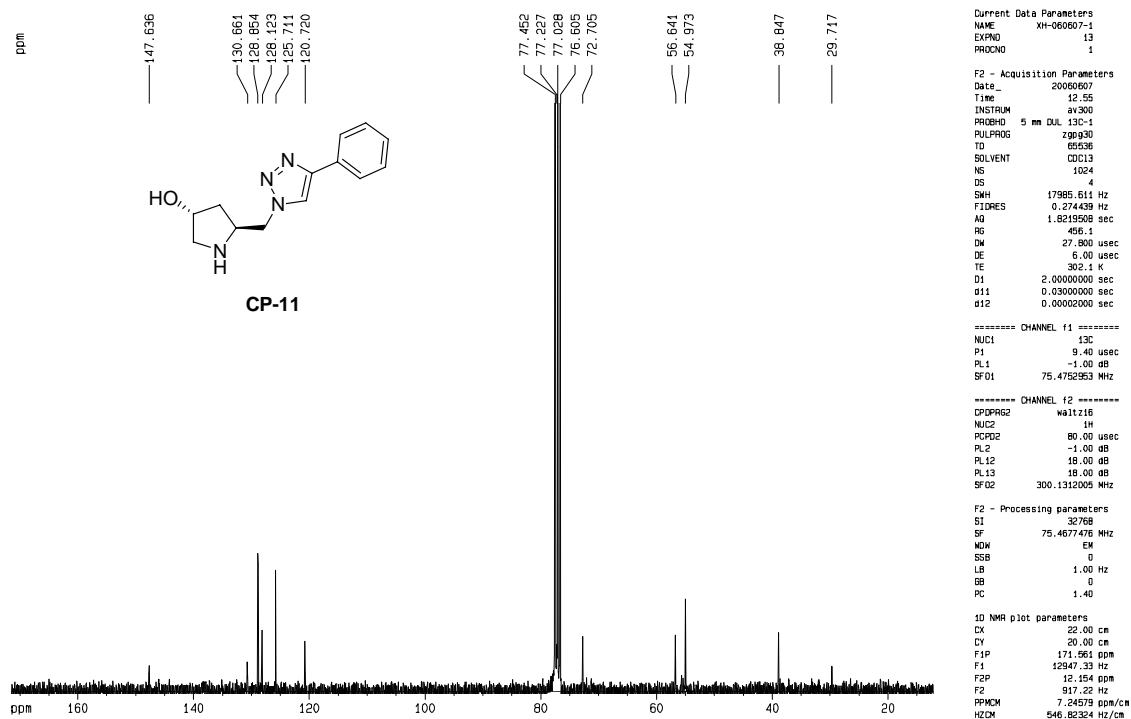
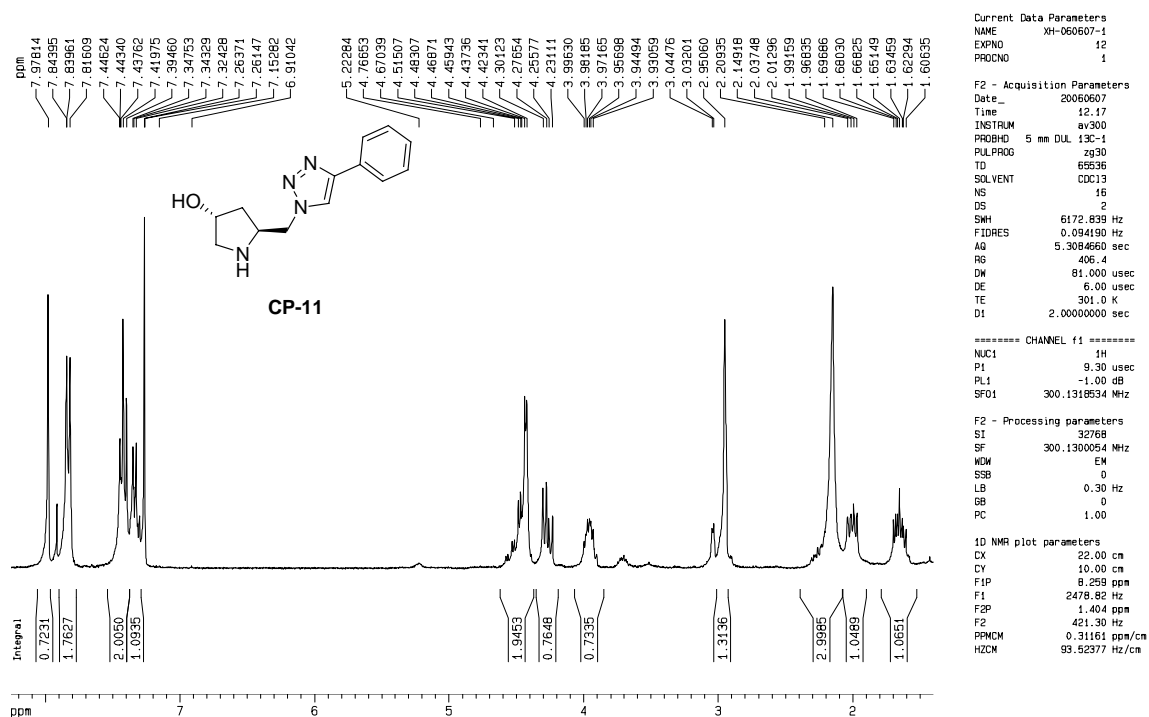
\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
CPDPRG2 waltz16  
NUC2 1H  
PCPD2 80.00 usec  
PL2 -1.00 dB  
PL12 18.00 dB  
PL13 18.00 dB  
SF02 300.1312005 MHz

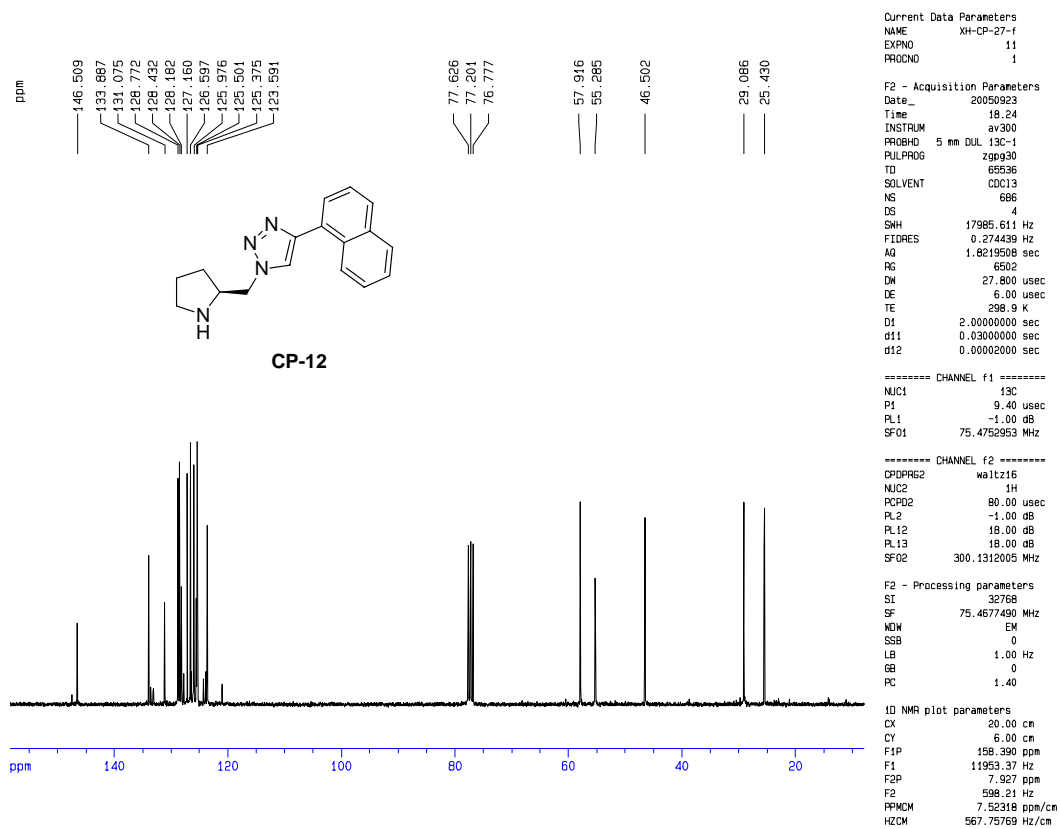
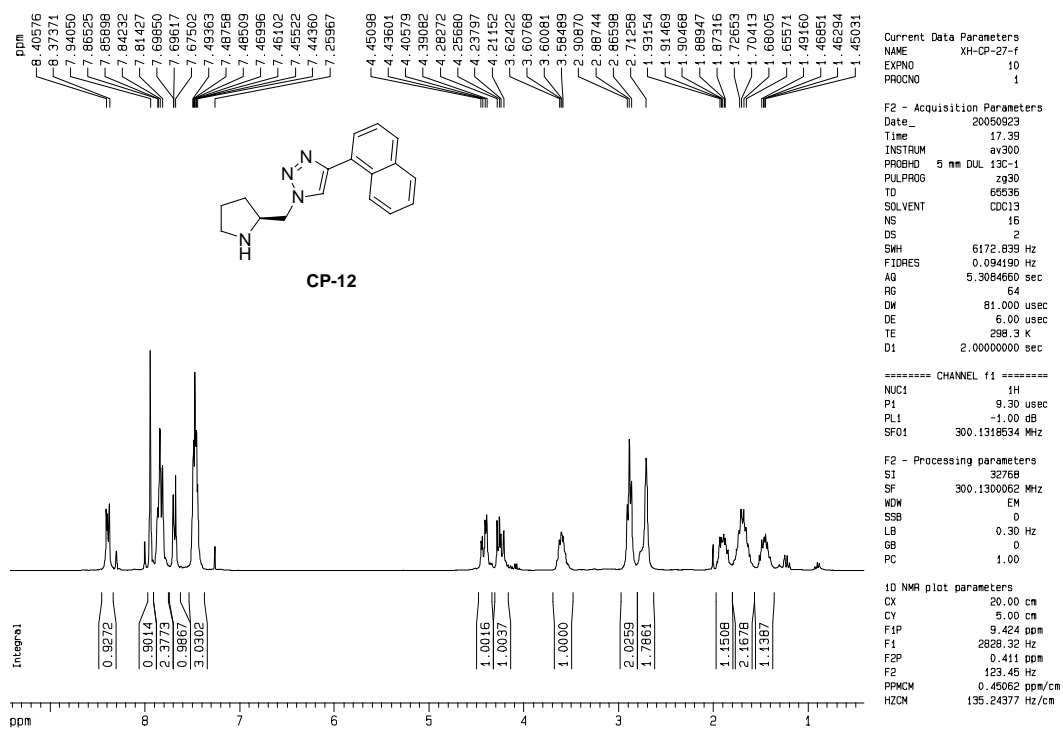
F2 - Processing parameters  
SI 32768  
SF 75.4678261 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

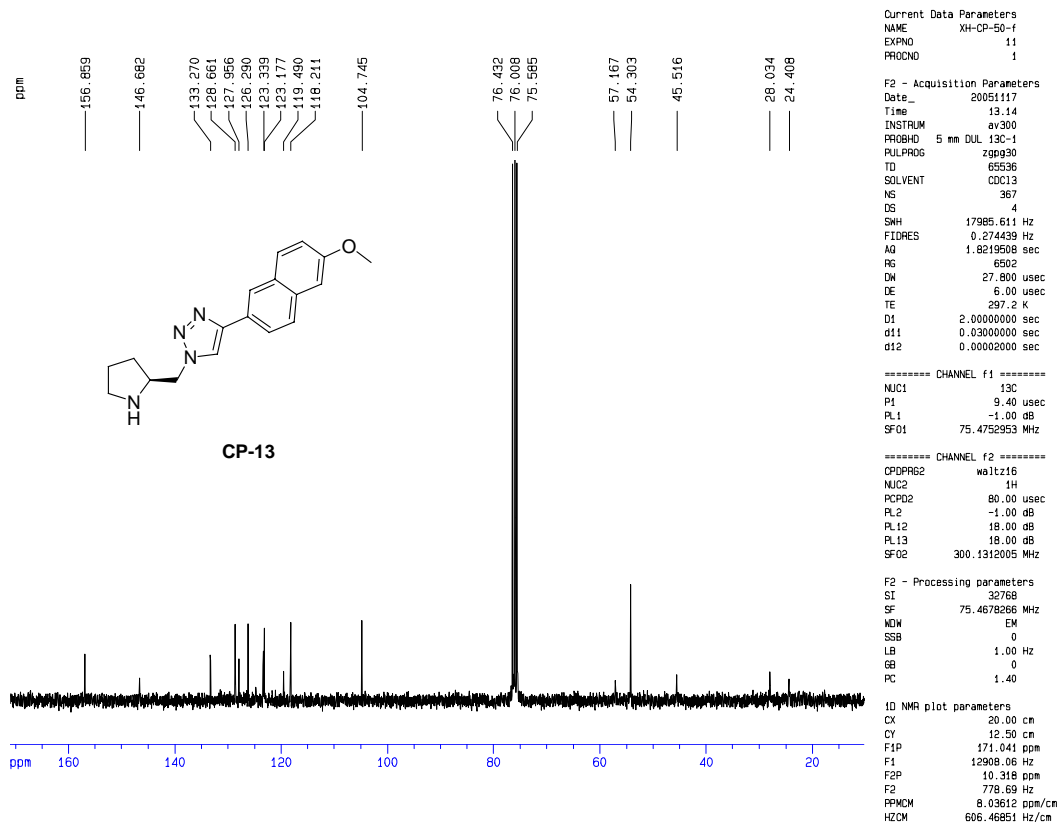
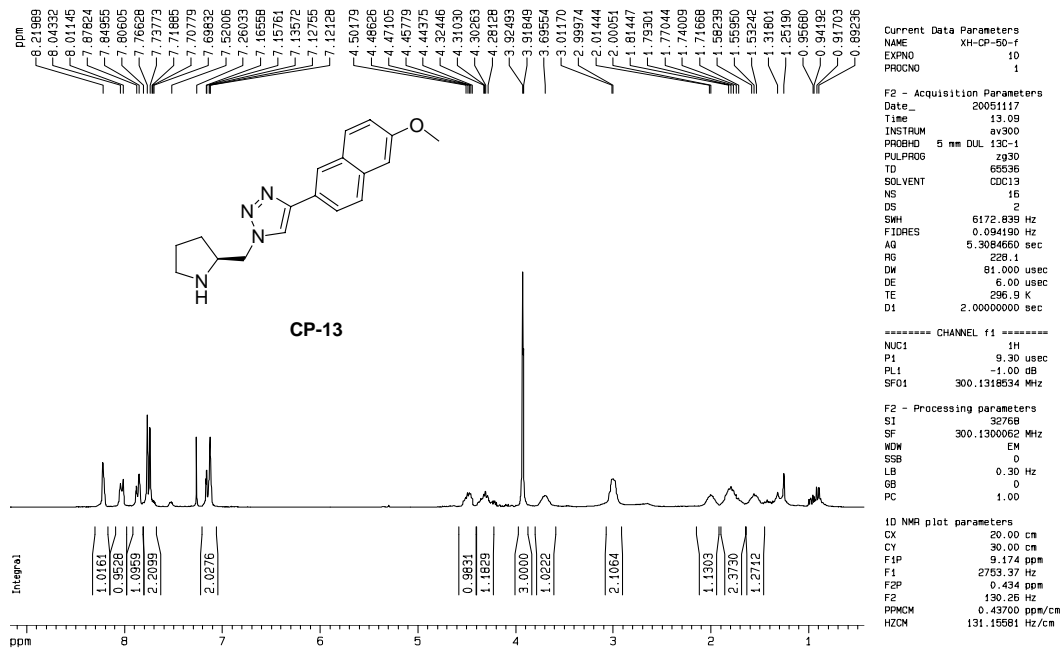
1D NMR plot parameters  
CX 22.00 cm  
CY 20.00 cm  
F1P 173.414 ppm  
F1 133067.28 Hz  
F2P 4.800 ppm  
F2 362.28 Hz  
PMCM 7.56427 ppm/cm  
HZCM 578.40540 Hz/cm

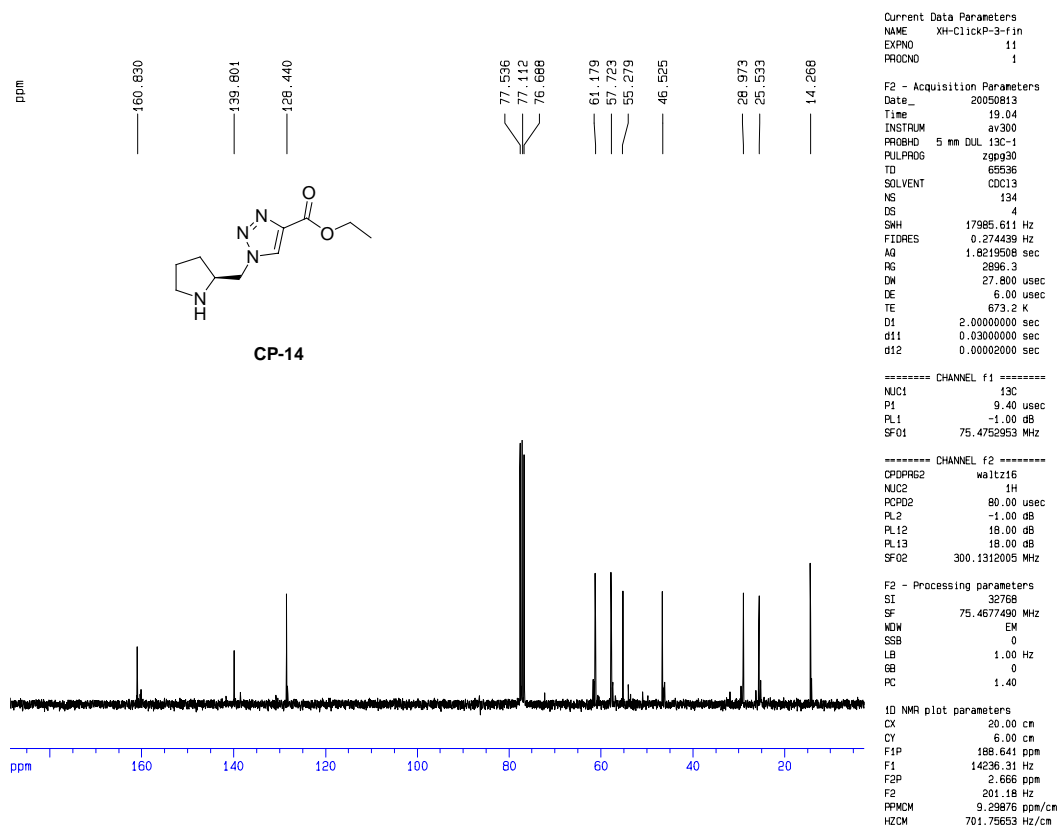
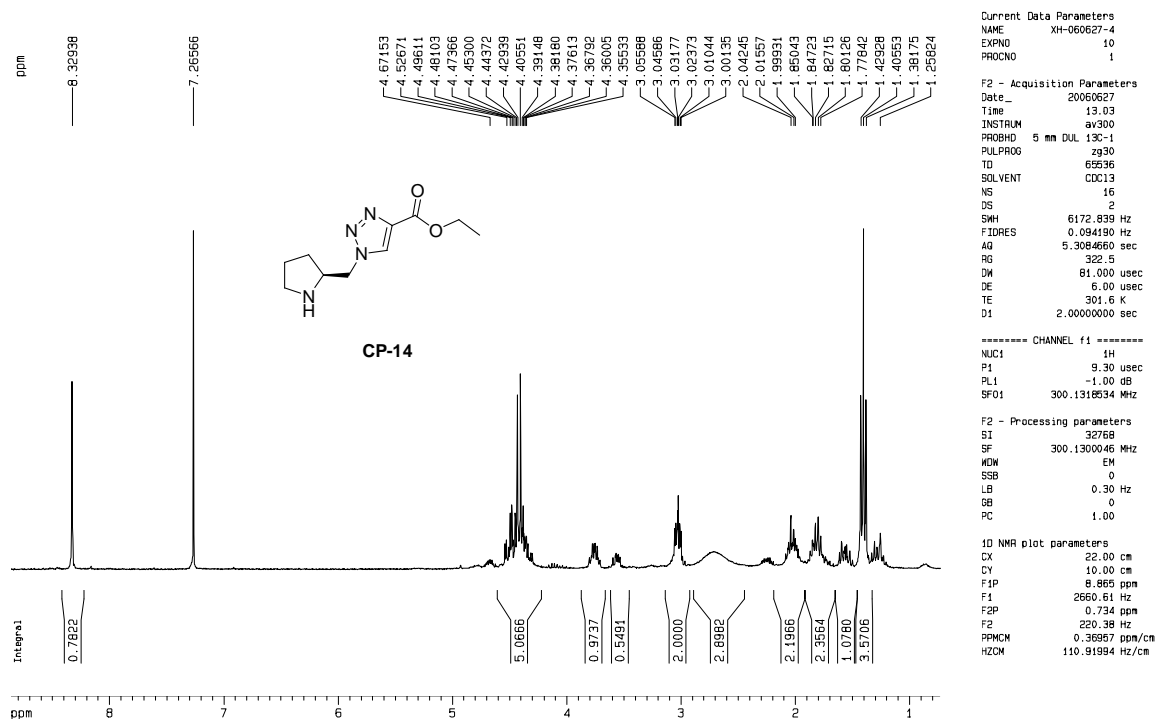


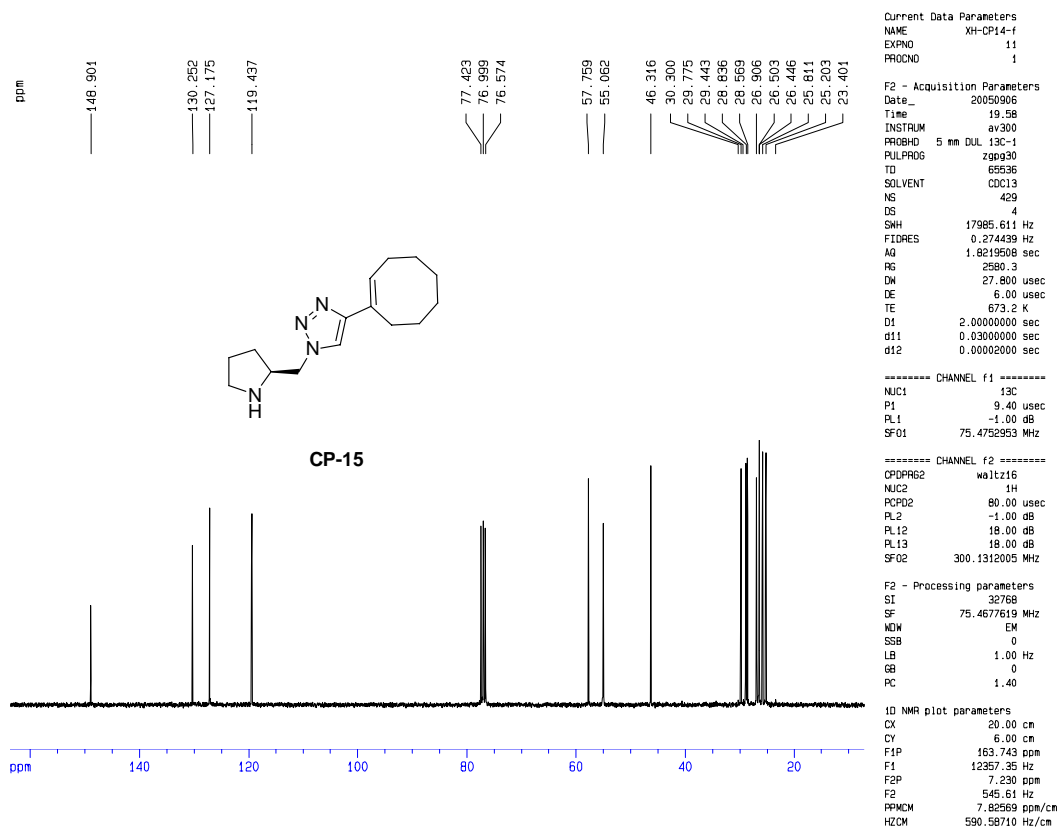
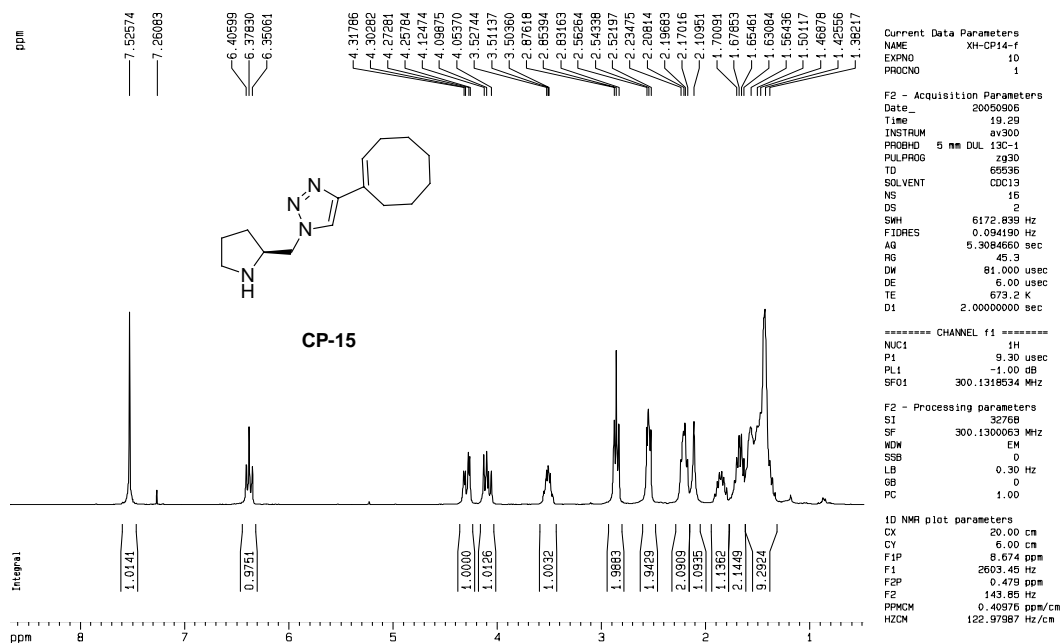


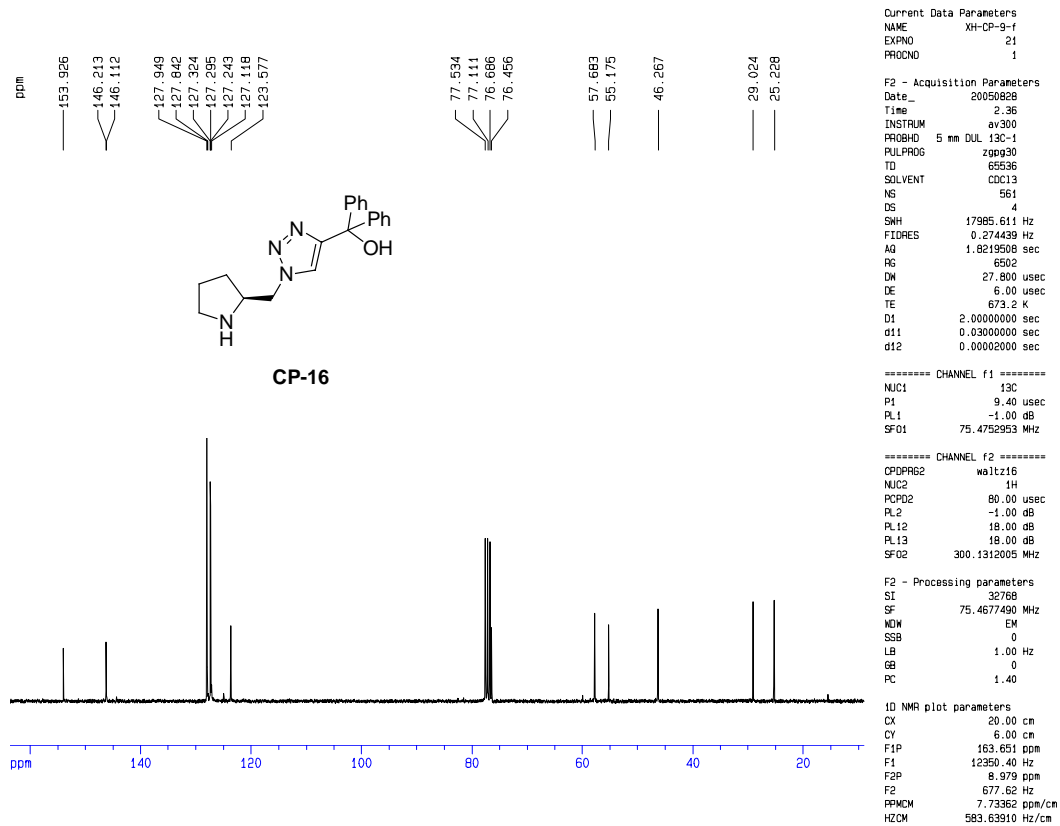
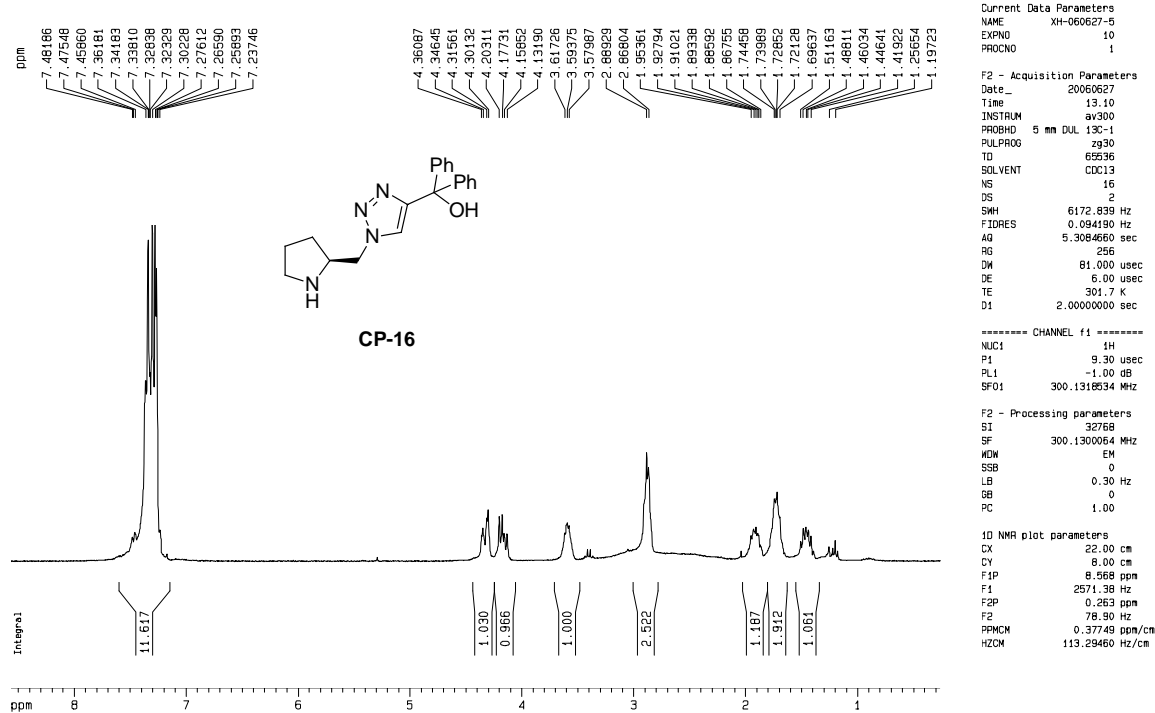


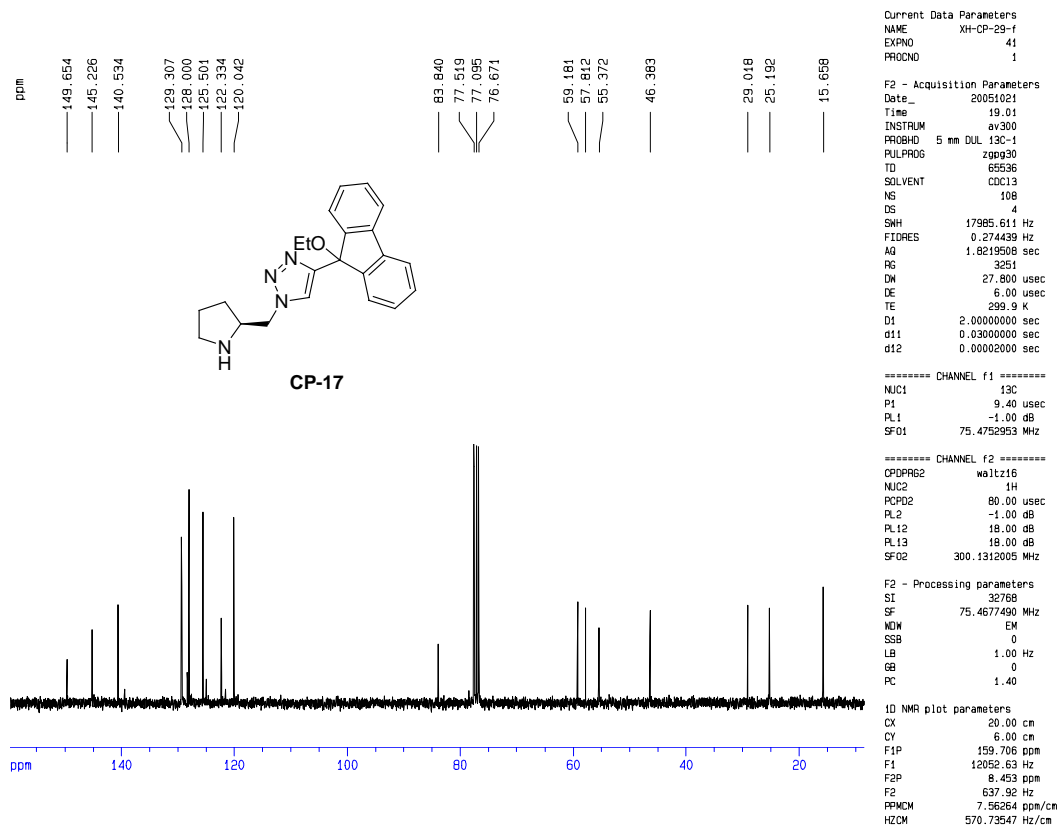
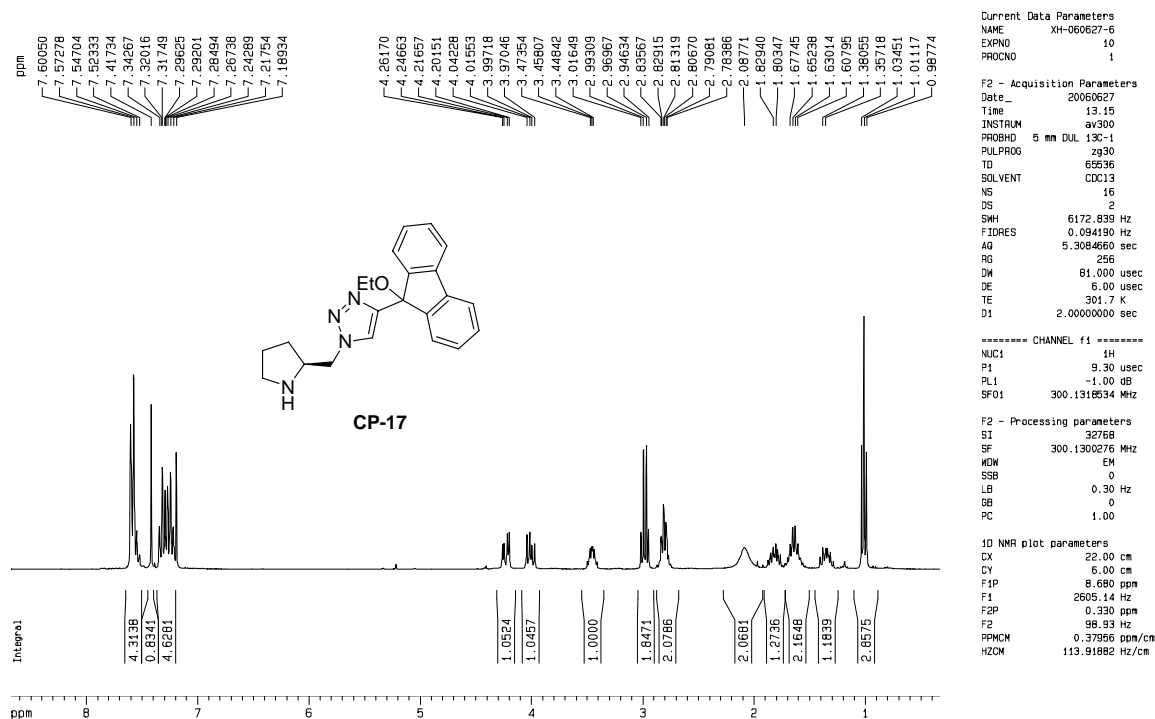




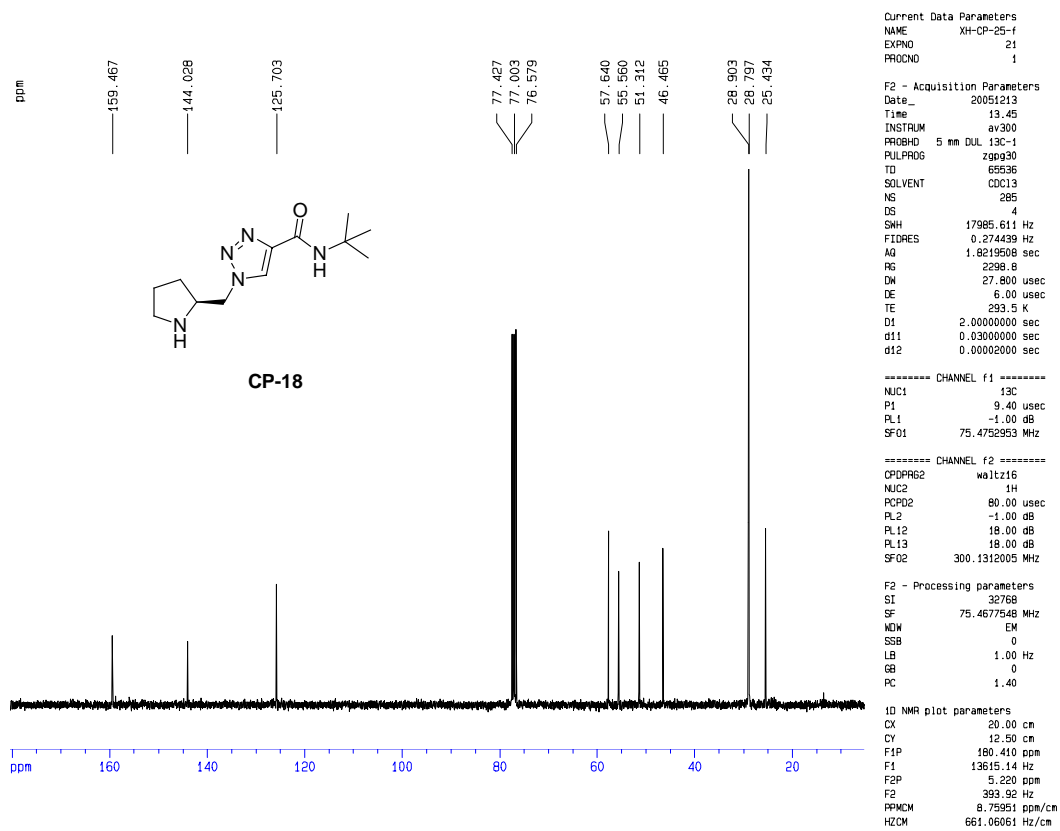
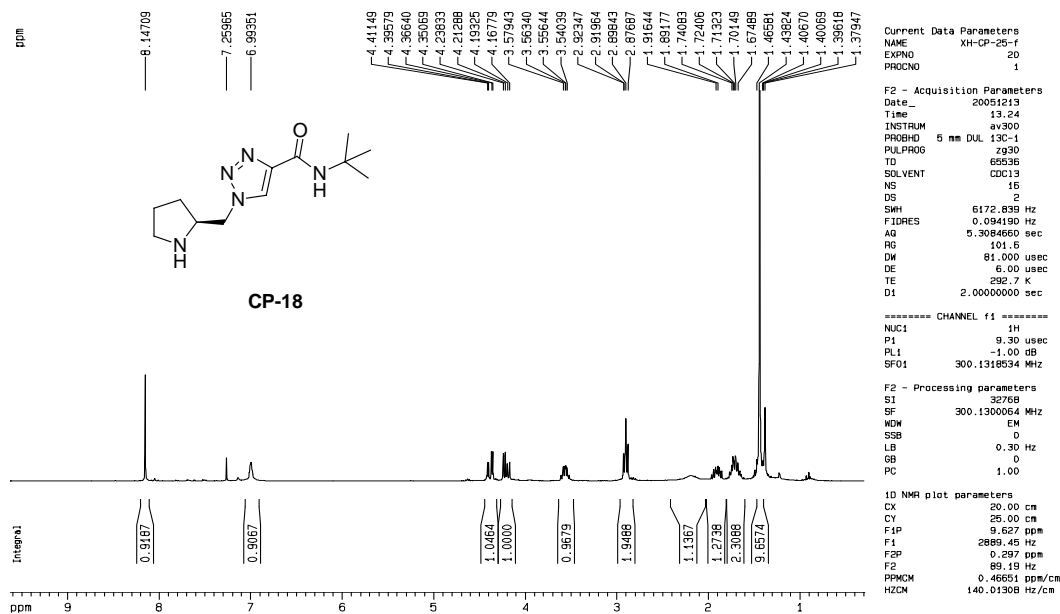


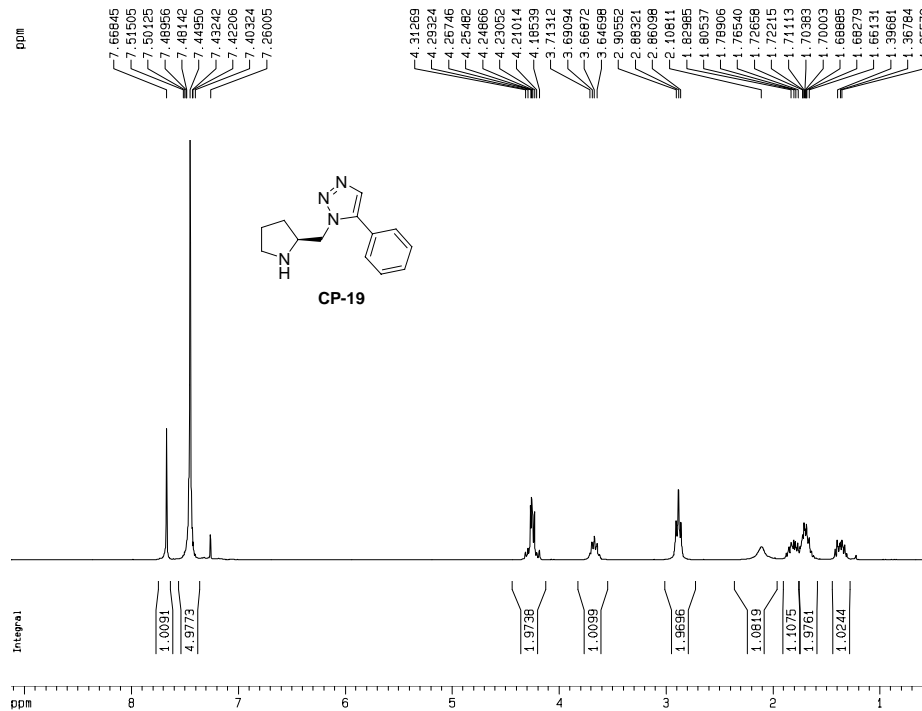












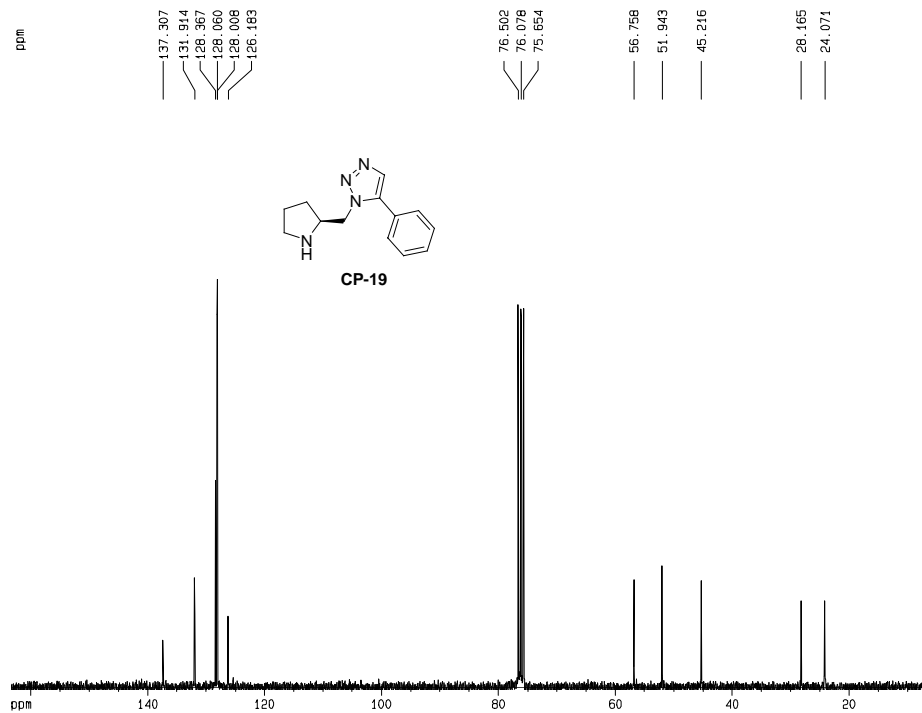
Current Data Parameters  
 NAME XH-15CP-1-3  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20051223  
 Time 13.23  
 INSTRUM av300  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 6172.839 Hz  
 FIDRES 0.094190 Hz  
 AQ 5.3084660 sec  
 RG 114  
 DW 81.000 usec  
 DE 6.00 usec  
 TE 294.4 K  
 D1 2.00000000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 1H  
 P1 9.30 usec  
 PL1 -1.00 dB  
 SF01 300.1318534 MHz

F2 - Processing parameters  
 SI 32768  
 SF 300.1300064 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

1D NMR plot parameters  
 CX 22.00 cm  
 CY 10.00 cm  
 F1P 9.128 ppm  
 F1 2739.56 Hz  
 F2P 0.501 ppm  
 F2 150.51 Hz  
 PPMCM 0.39211 ppm/cm  
 HZCM 117.68408 Hz/cm



Current Data Parameters  
 NAME XH-15CP-1-3  
 EXPNO 11  
 PROCNO 1

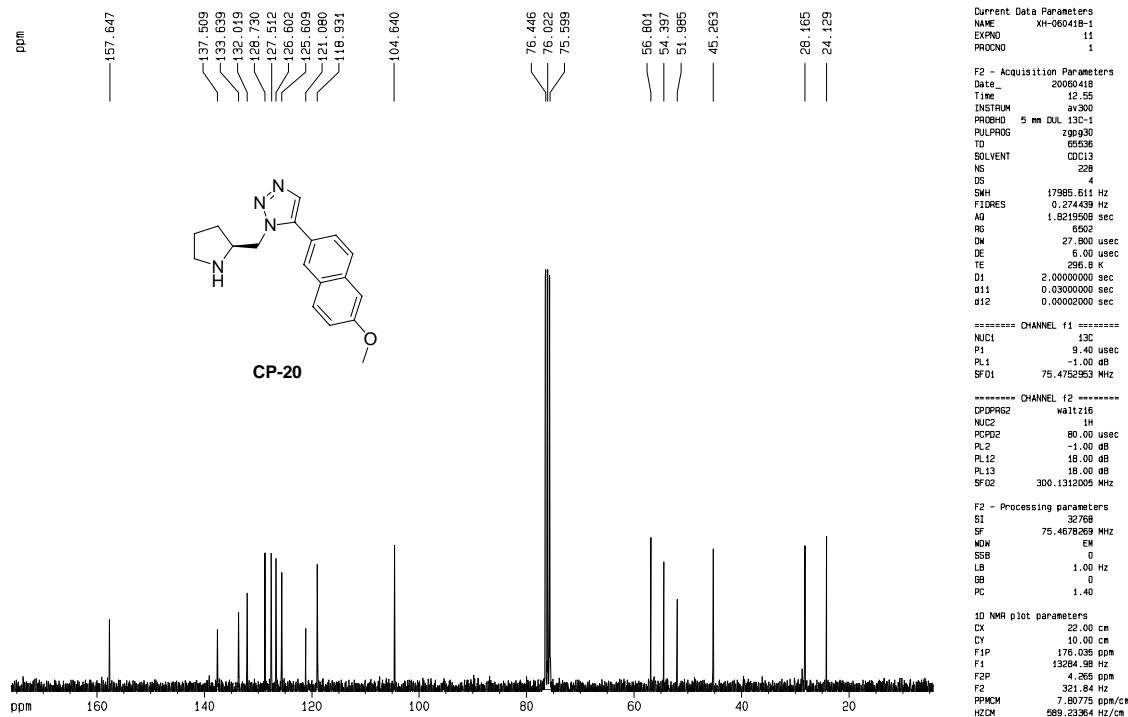
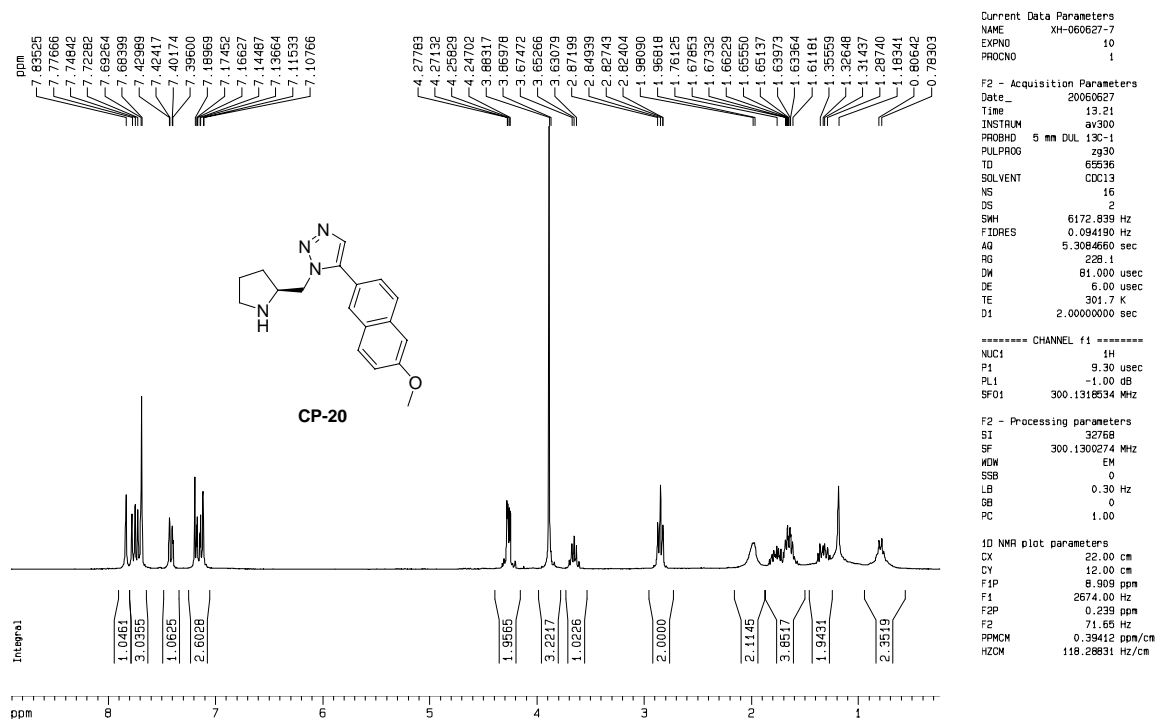
F2 - Acquisition Parameters  
 Date\_ 20051223  
 Time 13.27  
 INSTRUM av300  
 PROBHD 5 mm DUL 13C-1  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 140  
 DS 4  
 SWH 17985.511 Hz  
 FIDRES 0.274439 Hz  
 AQ 1.8219508 sec  
 RG 9196.2  
 DW 27.800 usec  
 DE 6.00 usec  
 TE 294.6 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 d12 0.00002000 sec

\*\*\*\*\* CHANNEL f1 \*\*\*\*\*  
 NUC1 13C  
 P1 9.40 usec  
 PL1 -1.00 dB  
 SF01 75.4752953 MHz

\*\*\*\*\* CHANNEL f2 \*\*\*\*\*  
 CPDPRG2 waltz16  
 NUC2 1H  
 PCPD2 80.00 usec  
 PL2 -1.00 dB  
 PL12 18.00 dB  
 PL13 18.00 dB  
 SF02 300.1312005 MHz

F2 - Processing parameters  
 SI 32768  
 SF 75.4678263 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

1D NMR plot parameters  
 CX 22.00 cm  
 CY 10.00 cm  
 F1P 163.416 ppm  
 F1 12332.67 Hz  
 F2P 5.587 ppm  
 F2 421.67 Hz  
 PPMCM 7.17404 ppm/cm  
 HZCM 541.40918 Hz/cm



# <sup>1</sup>H NMR spectra for the Michael products

